

FOURTEENTH INTERNATIONAL SCHOOL ON VACUUM, ELECTRON AND ION TECHNOLOGIES

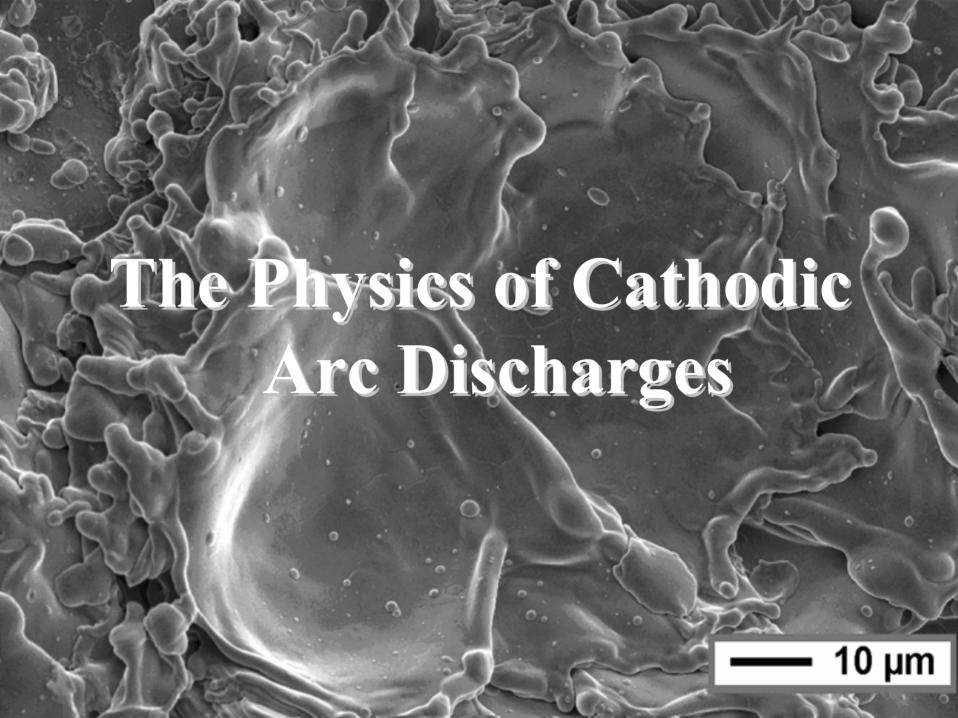
12-16 September 2005 Sunny Beach, Bulgaria

Cathodic arc plasma deposition: From fractal spots to energetic condensation

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Introduction: Definitions, Measurements & Phenomenology



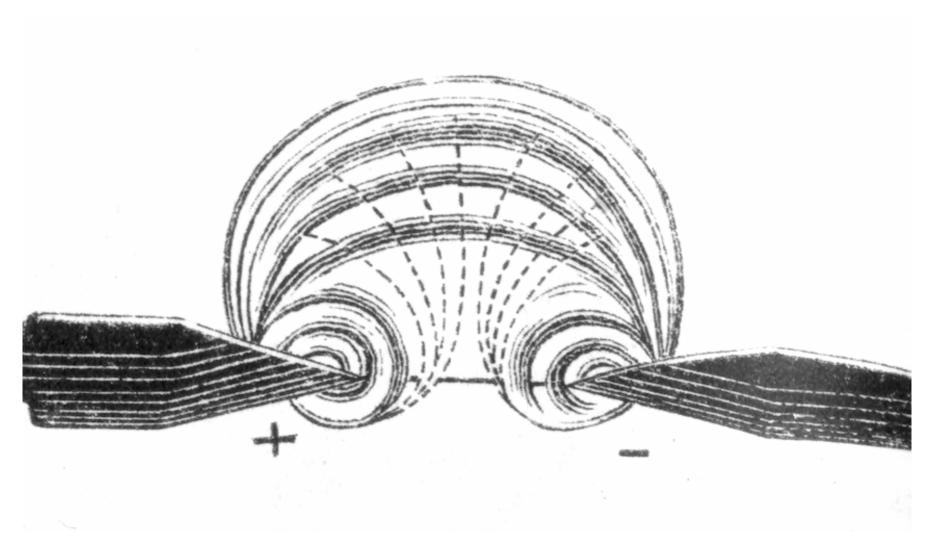
What is a cathodic (vacuum) arc?

□ Arc discharge:

- Electrical discharge through a plasma, characterized by
 - Relatively high current (typically > 5 A)
 - Relatively low voltage (typically < 50 V)
 - collective electron emission mechanism at the cathode
- □ "Vacuum" arc discharge:
 - Arc discharge whose plasma is produced at electrodes
- □ *Cathodic* (vacuum) arc discharge:
 - Vacuum arc discharge whose plasma is produced at cathode spots
- □ *Anodic* (vacuum) arc discharge:
 - Vacuum arc discharge whose plasma is produced from evaporating anode material



Arc Discharge







Electron Emission Mechanisms

Physics problem:

- □ Electron transfer over the cathode's potential barrier Nature's solution:
- □ "collective" electron emission mechanisms:
 - Thermionic emission
 - Field emission
 - Thermo-field emission
 - Explosive emission (this includes cathode plasma)
- □ As opposed to "individual" e-emission mechanisms:
 - Secondary electron emission by primary particle impact:
 - Ion
 - Electron
 - Excited / energetic atom
 - Photon

glow discharge

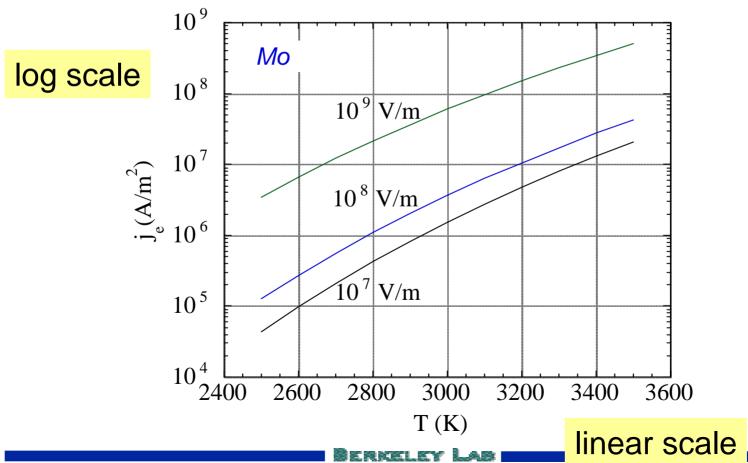
arc discharge

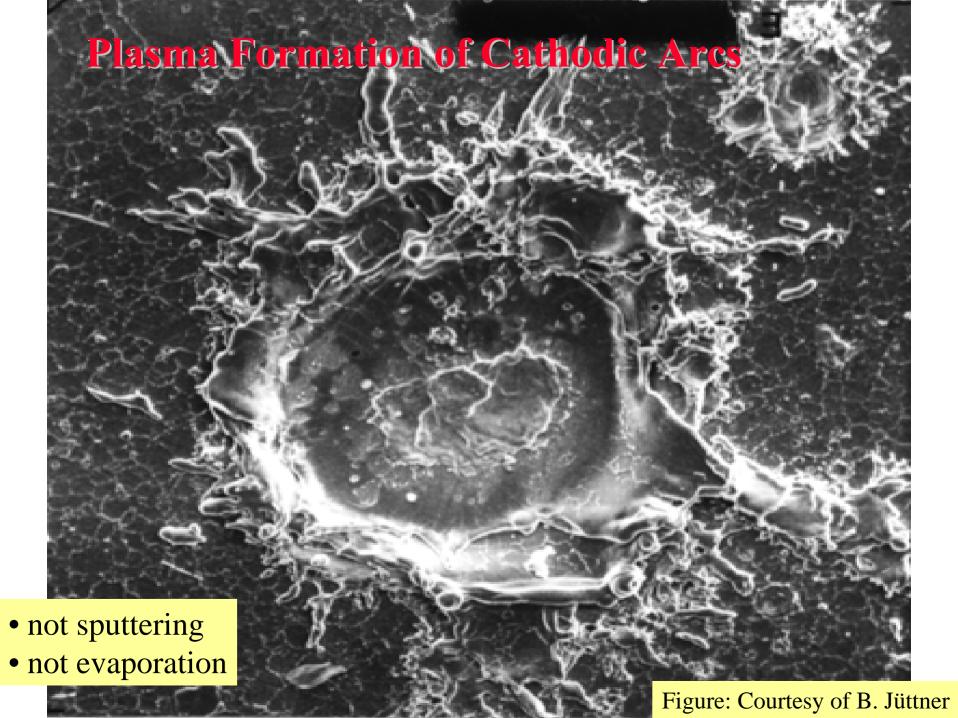




Thermofield Electron Emission

□ Current density of thermofield emission is necessarily associated with great power density → plasma formation can become explosive in nanosecond time scale







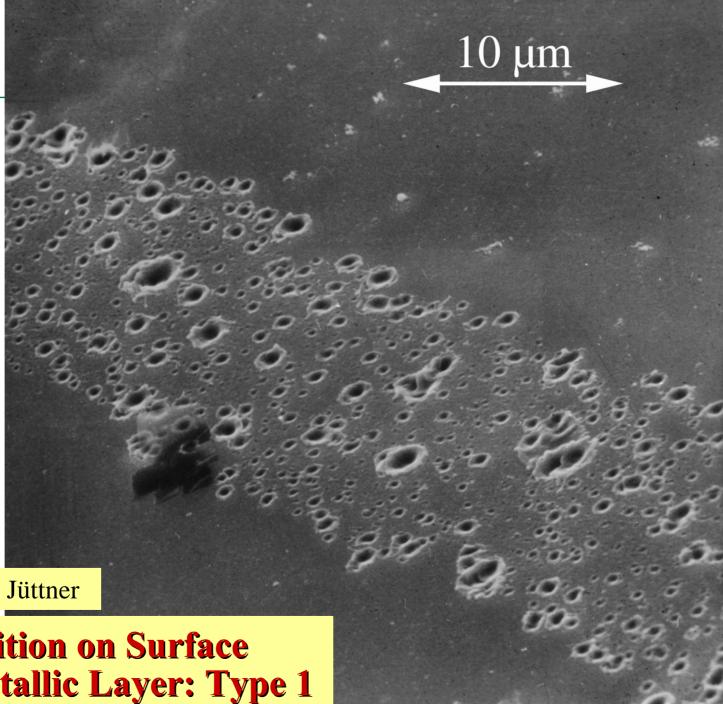


photo courtesy of B. Jüttner

Spot Ignition on Surface with Non-metallic Layer: Type 1



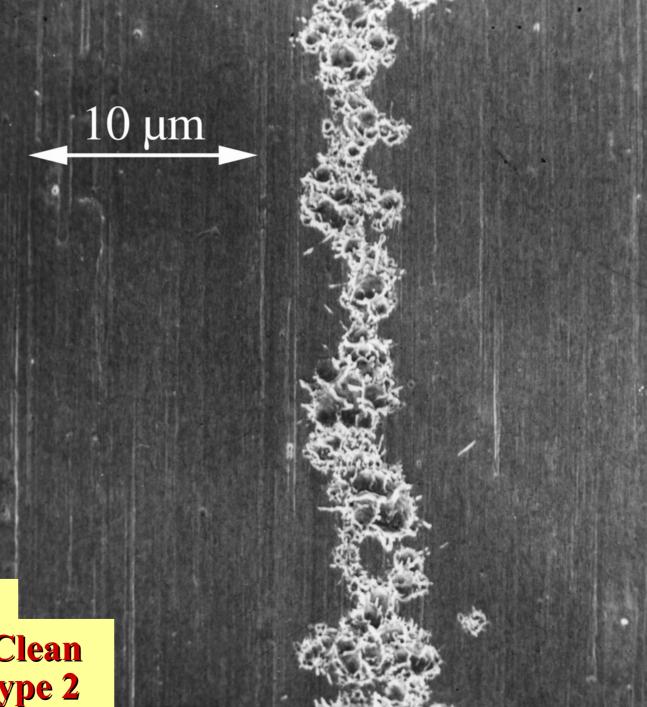
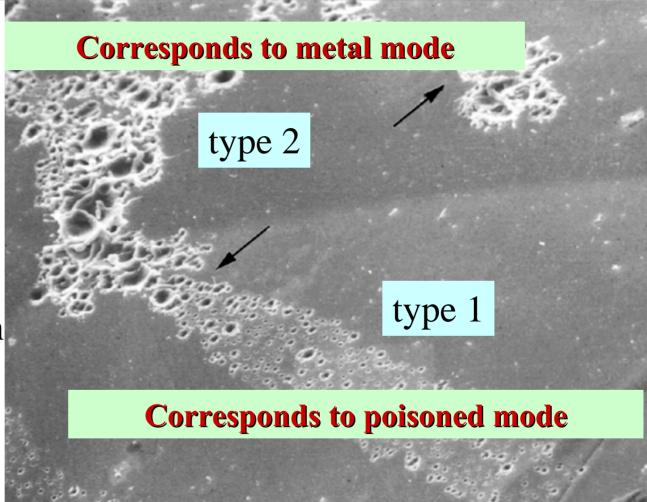


photo courtesy of B. Jüttner

Spot Ignition on Clean Metal Surface: Type 2

The Experimental Basis: Cathode Erosion and Plasma Formation

- □ arc spots / spot fragments leave crater traces
- ☐ type or mode depends on surface condition



from A. E. Guile, B. Jüttner, ZIE Preprint 80-2, Berlin, 1980

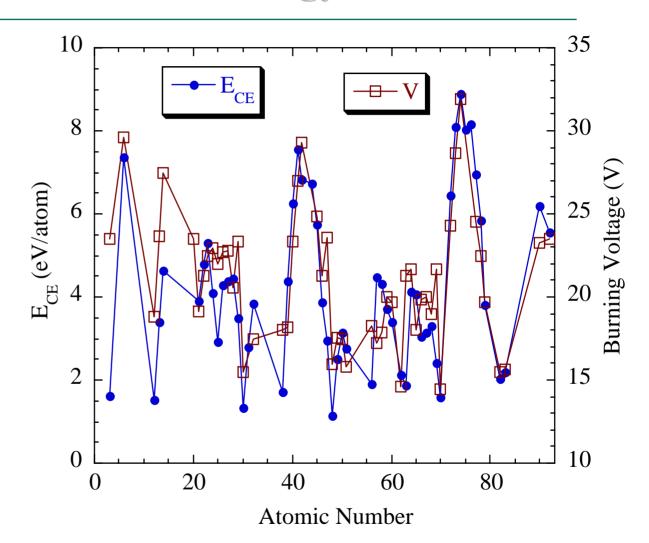
 $10~\mu\mathrm{m}$



Cohesive Energy Rule

Energy balance consideration:

There is a direct correlation between cohesive energy of the cathode solid and burning voltage of cathodic arc



cohesive energy = energy needed to free an atom from the solid



Properties of Cathodic Arc Plasmas

- \square Plasma expands from near solid state density (10²⁷ m⁻³) in the cathode spot to very rarified plasma far from spot (e.g. down to 10^{14} m^{-3}):
- ☐ for "large" distances from spot: plasma is in non-equilibrium
- □ Jüttner's formula: in absence of magnetic field and for

$$r > 100 \ \mu m$$

$$n \approx \gamma I_{arc} / r^2$$

□ For copper cathode: $\gamma \approx 10^{13} \text{ A}^{-1} \text{m}^{-1}$

$$\gamma \approx 10^{13} \text{ A}^{-1} \text{m}^{-1}$$

- □ electron temperature near spot 2-4 eV

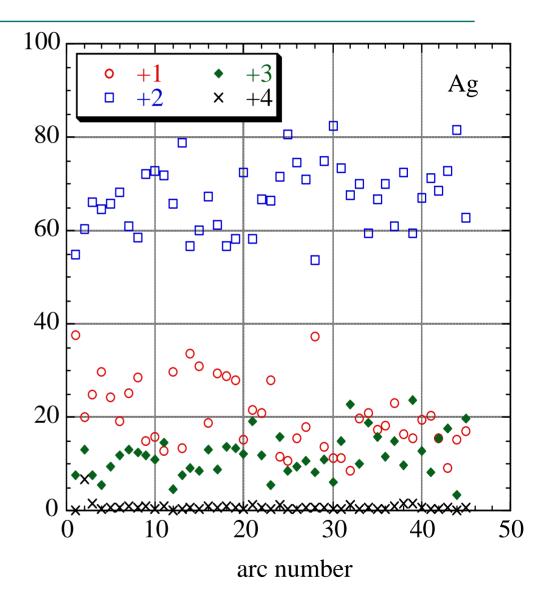
$$\square$$
 Average ion velocity $v_i \approx 0.8 - 2.2 \times 10^4 \,\mathrm{m/s}$

Electron current > arc current (this is not a typo!)



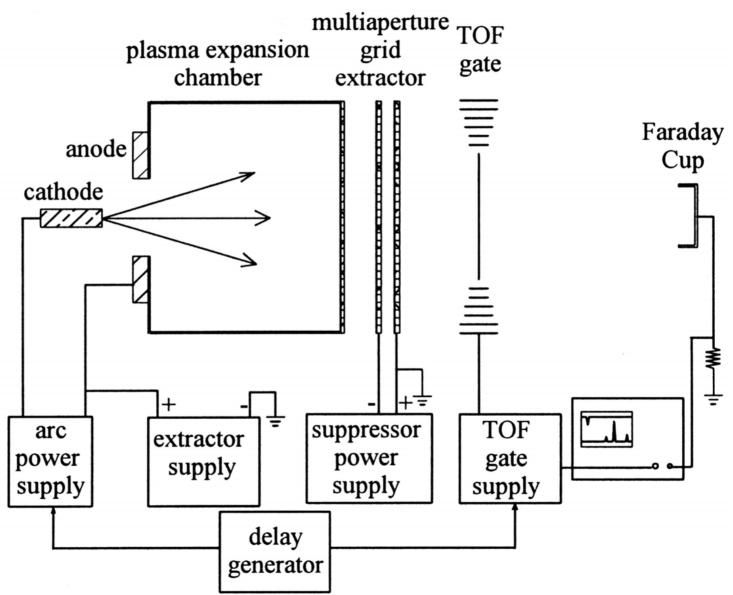
"Noise" or Fluctuations

- □ Noise due to the explosive nature of plasma production
- □ Noise is present in practically all parameters (voltage, density, temperature...)
- □ Noise is of little or no concern for plasma deposition (averaging effect)
- ☐ Example: CSD sampling of pulsed silver arc





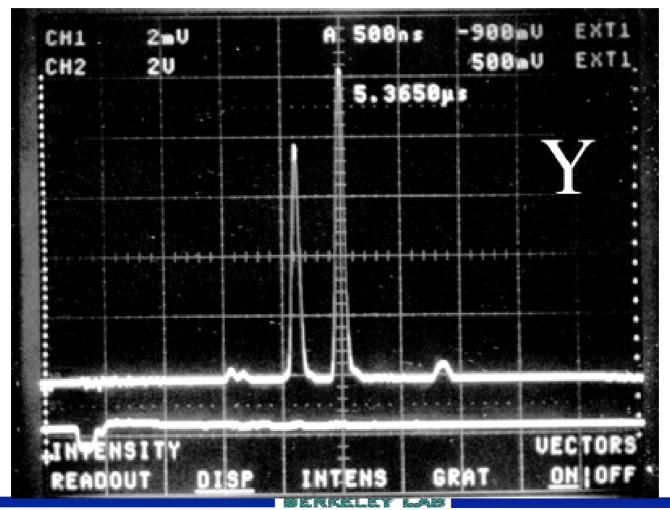
Ion Charge-State Spectrometry





Example of TOF Raw Data

□ Yttrium plasma, with ion charge states 1+, 2+, and 3+





Ion Charge State Distributions

- □ Ion charge state distributions (CSDs) of over 50 elements and alloys have been measured:
 - □ Mean ion charge state typically > 1; CSD is noisy

Brown, Rev. Sci. Instrum. 65 (1994) 3091

- □ CSD is enhanced at beginning of each arc discharge and reaches steady-state after about 100-200 µs
- CSD can be enhanced by
 - Magnetic field
 - High current (self field)
 - Current spikes

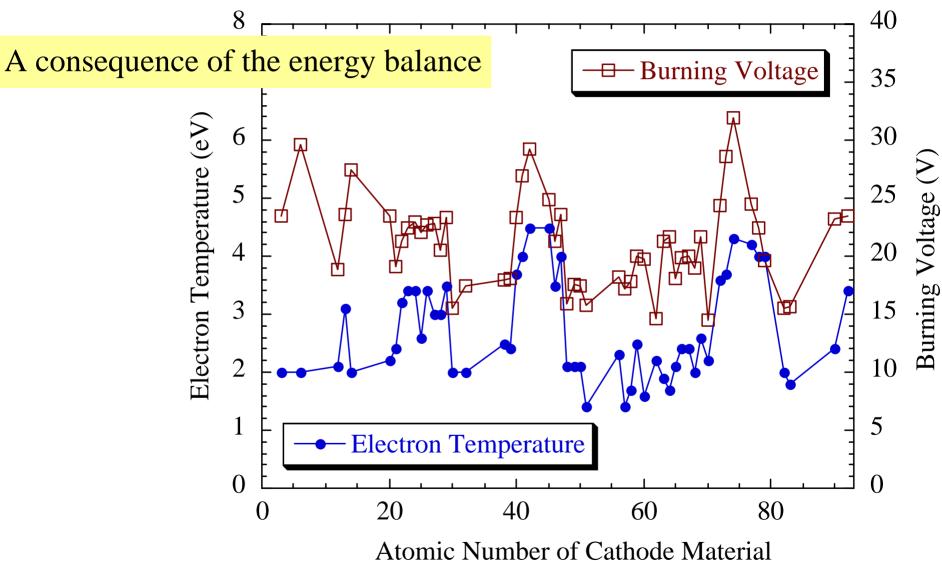
- Oks et al. IEEE Trans. Plasma Sci. **24** (1996) 1174
- □ CSD can be reduced by background gas
- □ Model of Local Saha Equilibrium includes charge state "freezing"

 A. Anders, Phys. Rev. E **55** (1997) 969

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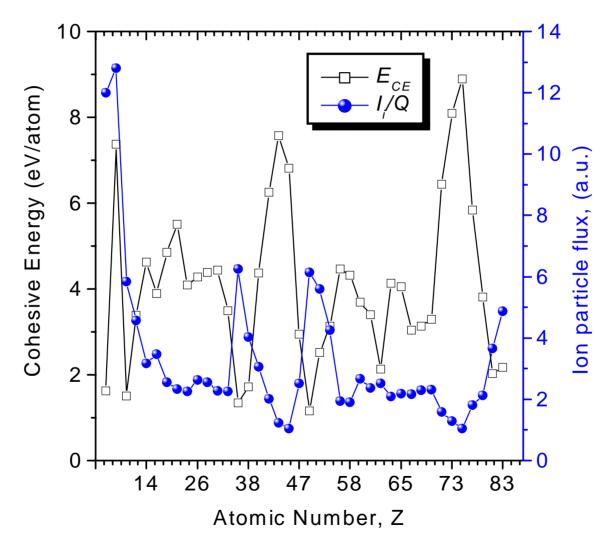


Secondary Relations Follow From Cohesive Energy Rule



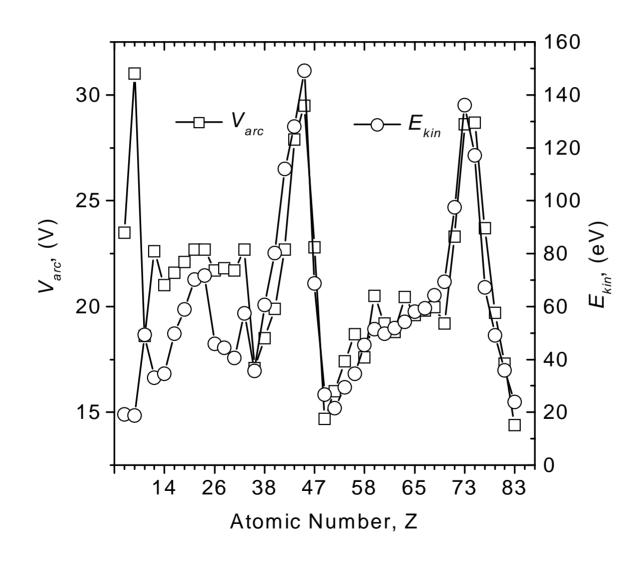


Erosion Rate and Cohesive Energy



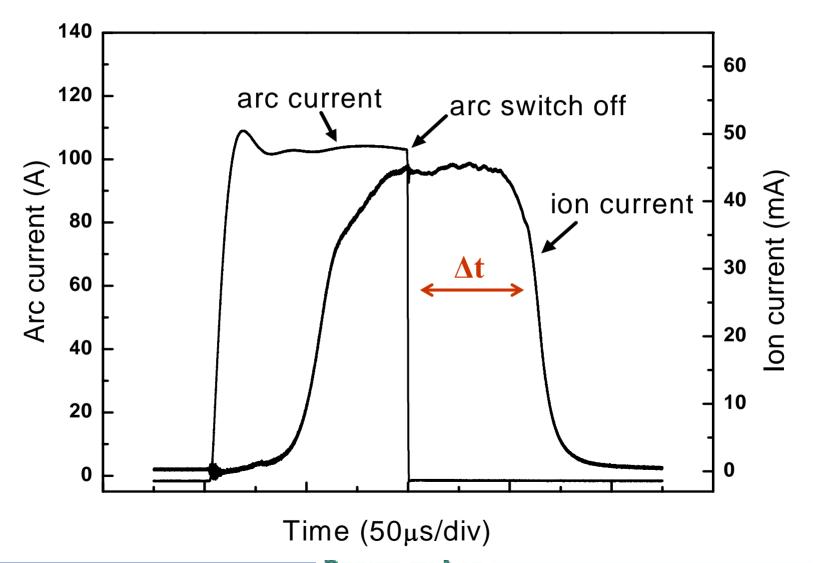


Cohesive Energy Rule Applied to Kinetic Ion Energy





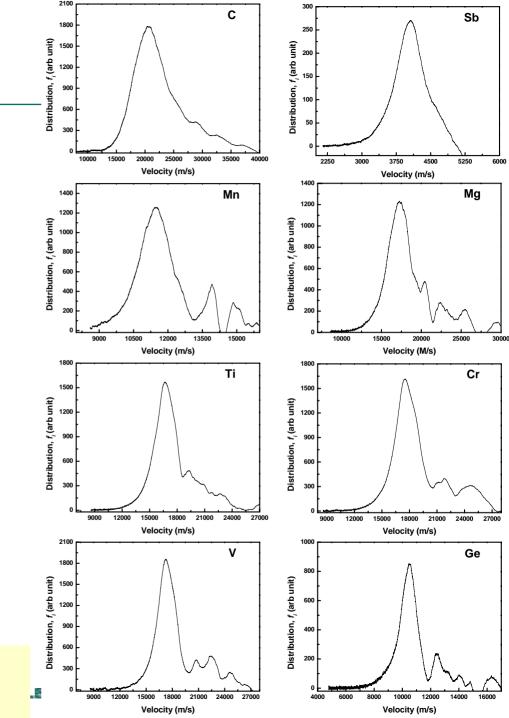
Time-of-Flight Measurement Setup with Current-Zero





TOF Results

- most distributions show *one* large peak
- indication that all charge states have about the same velocity i.e. kinetic energy is independent of charge state
- high energy peaks are uncertain and may be related to plasma instabilities



Byon and Anders, *J. Appl. Phys.* **93** (2003) 1899-1906

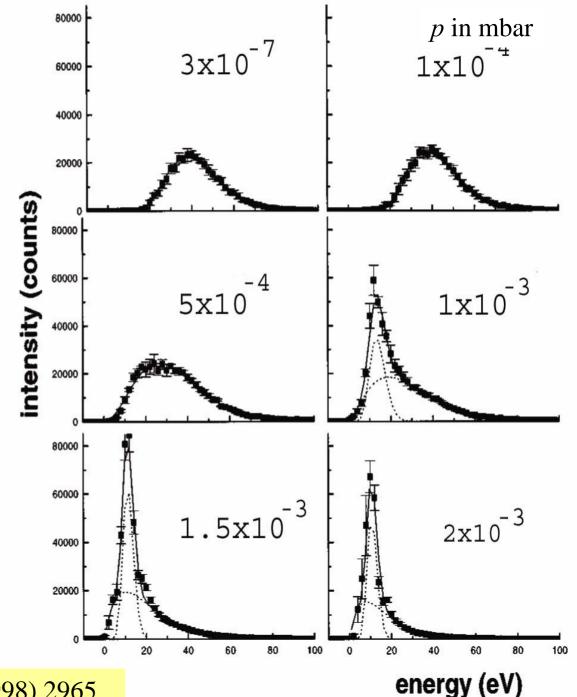


Kinetic Ion Energy With Background Gas

- □ Presence of gas causes changes in
 - □ plasma production
 - □ plasma transport
- □ changing surface condition of cathode, similar to "poisoning" of sputter target, issue of spot type
- □ Collisions with gas will shift ion energy distribution function to lower energy
- □ low-energy peak will appear, representing species that have lost energy in collision

Effect of Gas on Kinetic Energy of Metal Ions

- ☐ Example: Ti plasma in nitrogen
- □ method: mass selective energy analyzer



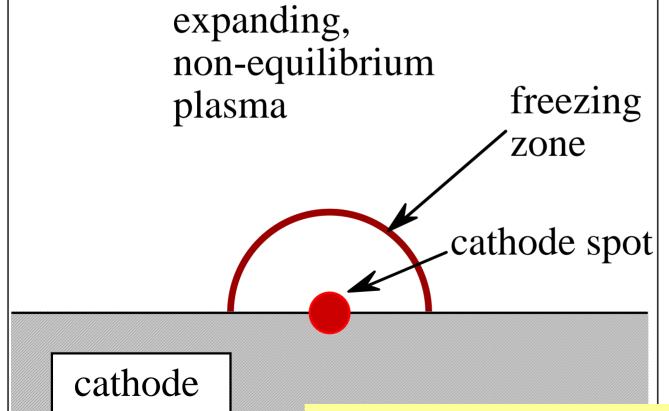


Theory & Models



Model of "Instantaneous Freezing"

□ Charge state spectrum reflects plasma condition at equilibrium ⇒ non-equilibrium transition zone, the "freezing zone" near cathode spot



Anders et al., J. Phys. D: Appl. Phys. 21 (1988) 213-215



Arc Spot Ignition

Local thermal run-away process leads to microexplosion and formation of extremely dense plasma:

High electric field, enhanced by

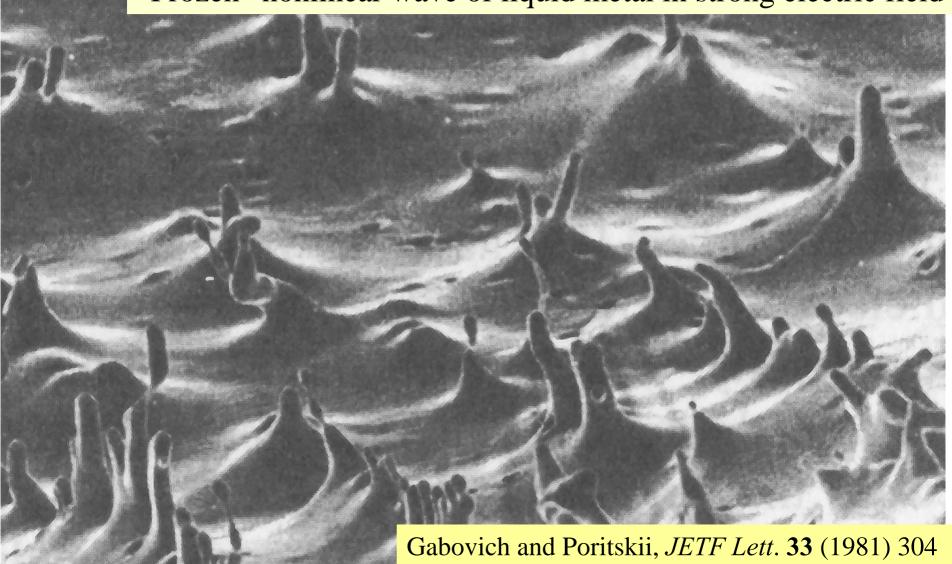
- 1. protrusion (e.g. roughness, previous arcing)
- 2. charged dielectrics (e.g. dust particles, flakes)
- 1. higher field leads to locally greater e-emission **feedback!**
- 2. Joule heat enhances temperature of emission site
- 3. higher temperature amplifies e-emission non-linearly

Runaway!



Explosive Emission and Arc Spot Ignition

"Frozen" nonlinear wave of liquid metal in strong electric field



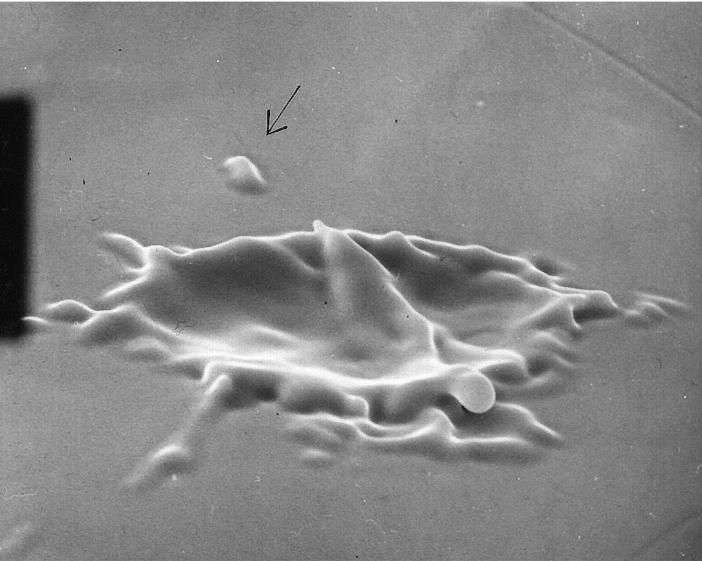


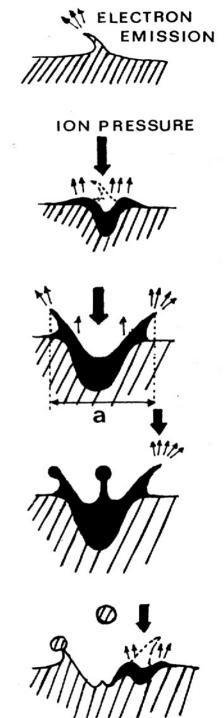
Macroparticle Formation: Response of a Liquid to Impulse Pressure





Self-Generation of Ignition Conditions



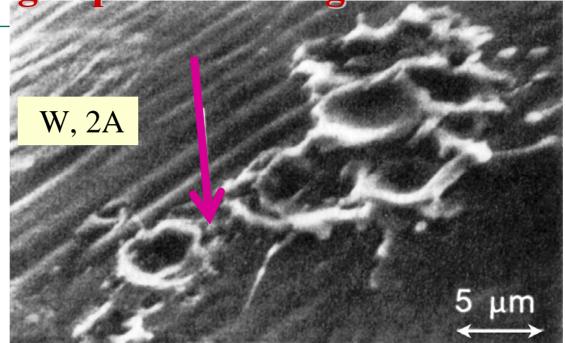


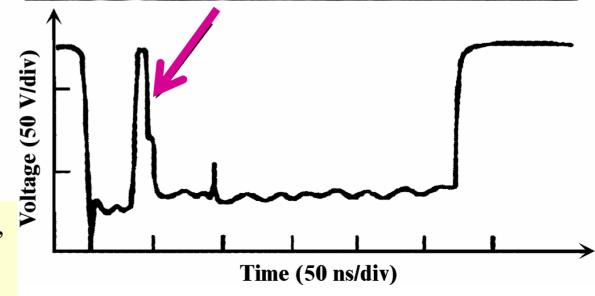
) ns discharge on Mo. Photo courtesy of B. Jüttner



Voltage Spike before Ignition

Extinction of emission center causes voltage to rise until new center is ignited





Puchkarev and Murzakayev, J. Phys. D 23 (1990) 26



Ignition and Types of Spot Motion

- □ *Spot motion*: Displacement of active spot by ignition of new spot and extinction of active spot
- □ for homogenous (uniform) surfaces: ignition probability follows laws of "diffusion-limited aggregation" resulting in "*random walk*"
- □ for non-uniform surfaces: ignition probability is higher at locations where local electric field is enhanced, especially by dielectric layers, charges, inclusions: ignition probabilities follows laws of "self-avoiding walk," i.e. does not ignite where ignition has happened before (conditioning effect!)
- □ if symmetry is broken by magnetic field: ignition probability is higher at locations where local electric field is enhanced via thinner sheath (higher density under plasma jets): "steered walk"



Effects of Layers and Magnetic Field on Spot Ignition

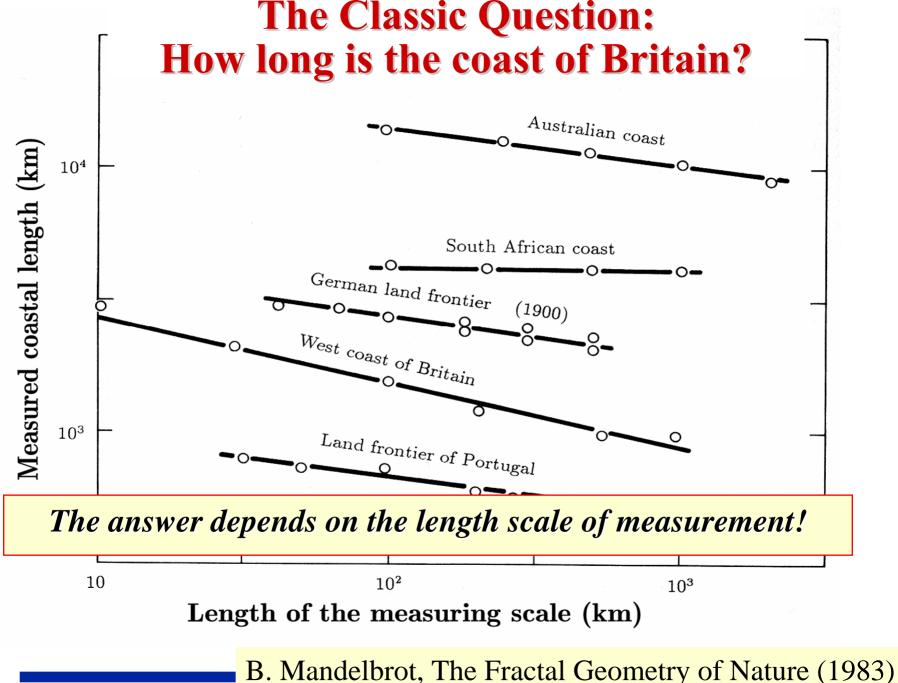
□ Both surface layers and magnetic field change probability distribution for spot ignition



□ these effects can be described in a single, generalized model: the *fractal model*.



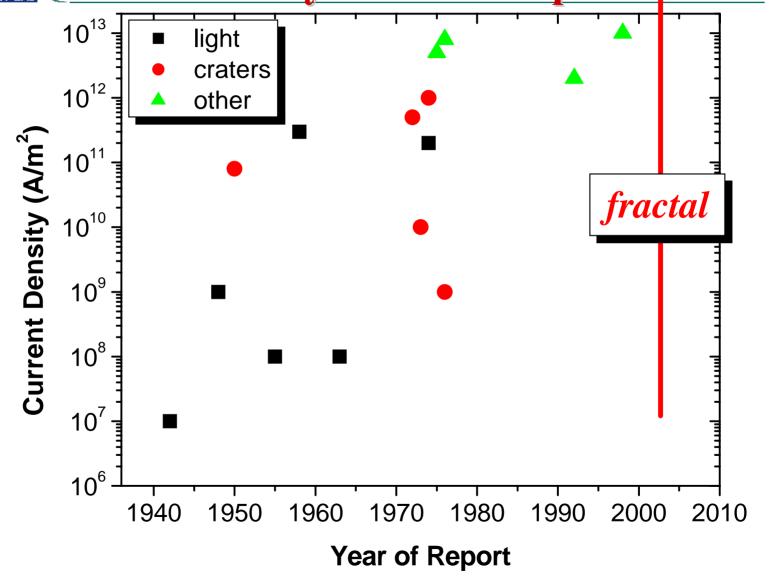
Fractals



André Anders, Plasma Applications Group



New Question: What is the current density of cathode spots?





Self-Similarity

- □ An object ("fractal") is self-similar (invariant with scaling) if it is reproduced by magnifying some portion of it.
- Self-similarity may be discrete or continuous, deterministic or probabilistic.
- □ Self-similarity can be mathematically exact or only approximate and asymptotical.

M. Schroeder, Fractals, Chaos, Power Laws, Freeman, New York, 2000



Fractals and Power Laws

Power laws are an abundant source of self-similarity.

The homogenous power law

$$f(x) = cx^{\alpha}$$

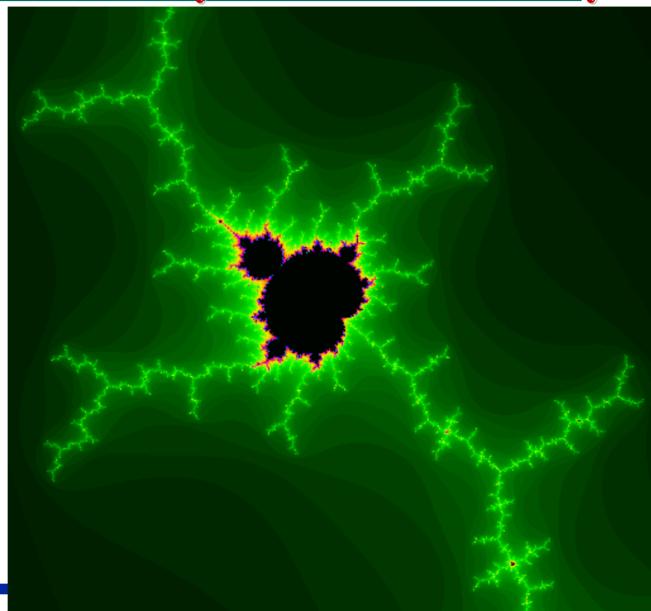
is self-similar because rescaling (multiplication with a constant) preserves that is proportional.

A fruitful approach to fractal modeling is to look for *power laws* describing the physical phenomena.



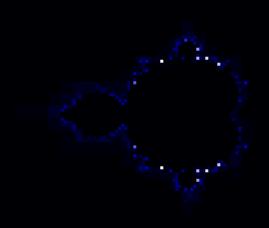
Example of Mathematically Exact Self-Similarity

Mandelbrot"Lightning"
and
Mandelbrot
Trees





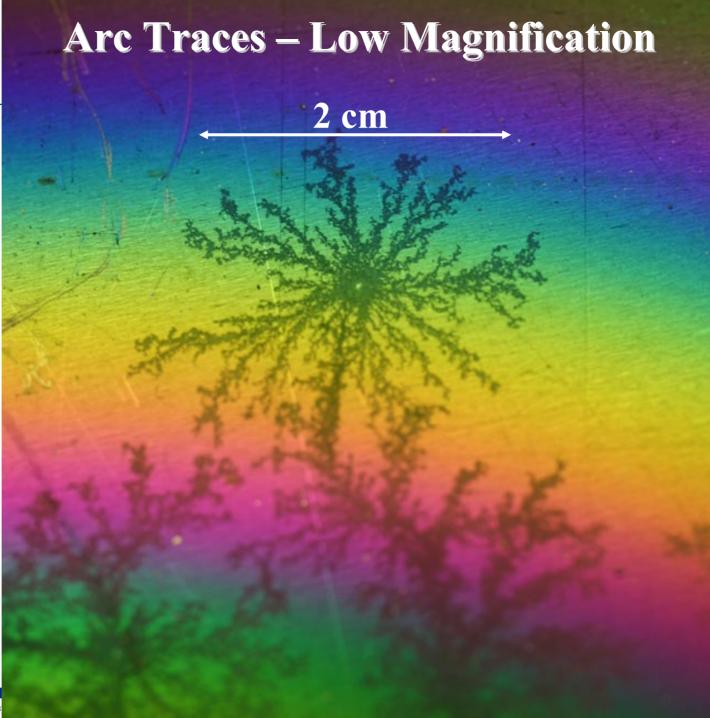
Example of Mathematically Exact Self-Similarity





Arcing on a SS shield coated with WO₃ (colors due to interference)

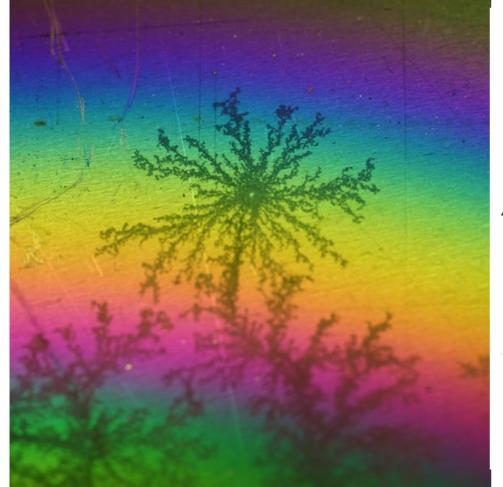
Traces are probabilistic fractal dimension ~ 1.7

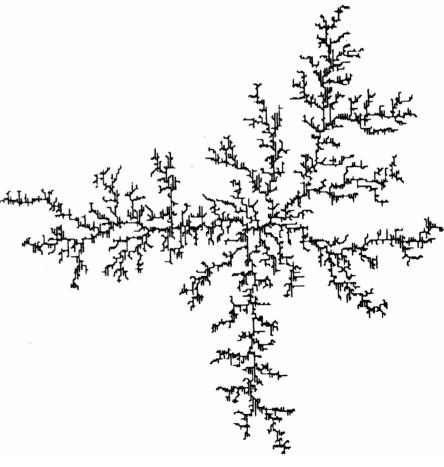




Fractal Model and Ignition

☐ The fractal approach to "*Diffusion-limited Aggregation*" is applicable to random walk model of spot motion; ignition of a new spot corresponds to attachment of a molecule to nucleation site







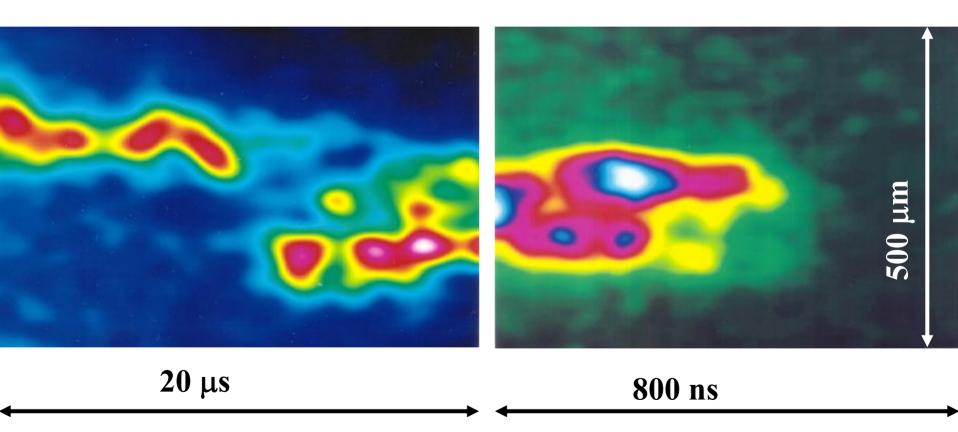
Ignition concept in Earlier History

- □ M.J. Druyvesteyn (1934): "It may be that the breakdown of the insulator [layer] causes the wandering of the cathode spot of an arc in some cases."
- □ J.D. Cobine (1938): "The discharge is influenced markedly by the condition of the copper cathode...this random variation [of the re-ignition voltage] is quite probably due to the variation in the in impurities at the cathode which influences the mechanism of arc re-ignition...



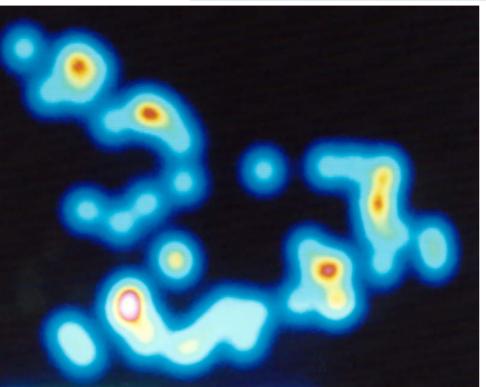
Temporal and Spatial Self-Similarity

Streak camera pictures at different time resolution (courtesy of B. Jüttner)





Simulation of Spot Light Emission

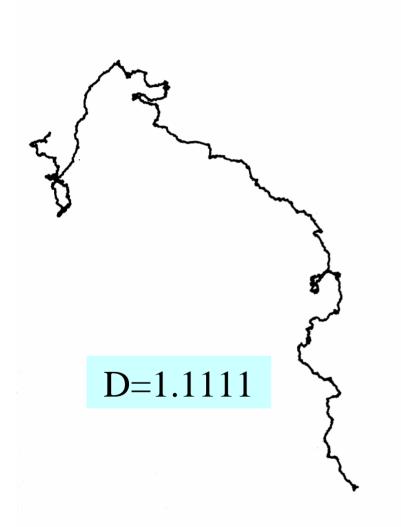


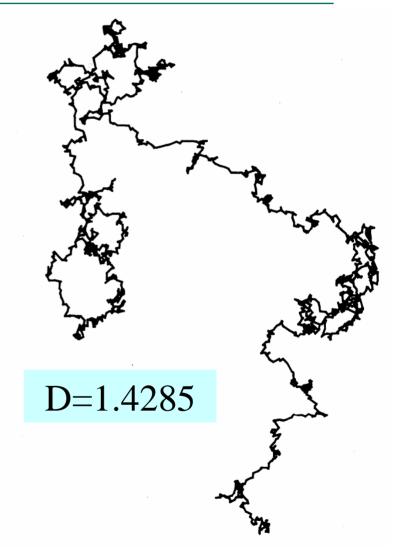
FWHM 10 μm, step=FWHM

FWHM 15 μm, step=FWHM/2



Random Motion: Probabilistic Fractal

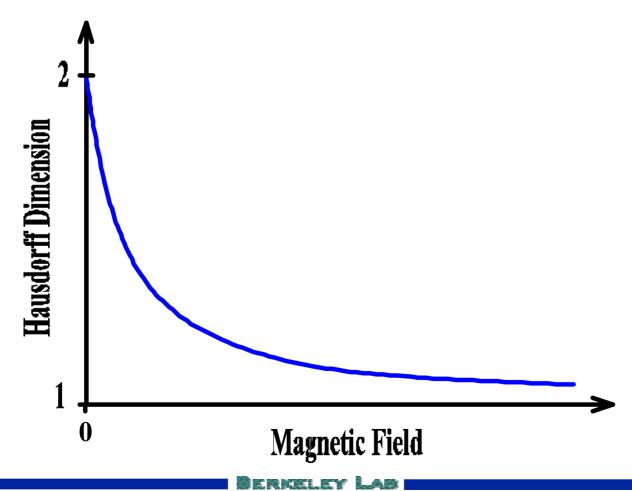






Fractal Dimension of Spot Motion

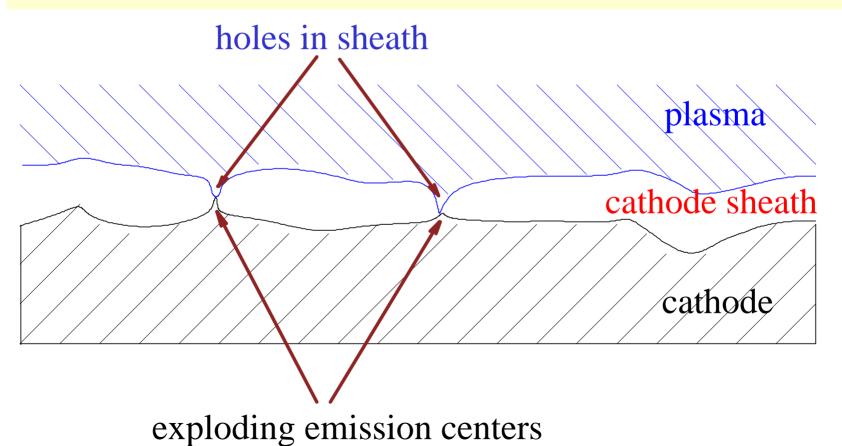
Transition from Random Motion to Steered Motion can be associated with a reduction of the fractal dimension

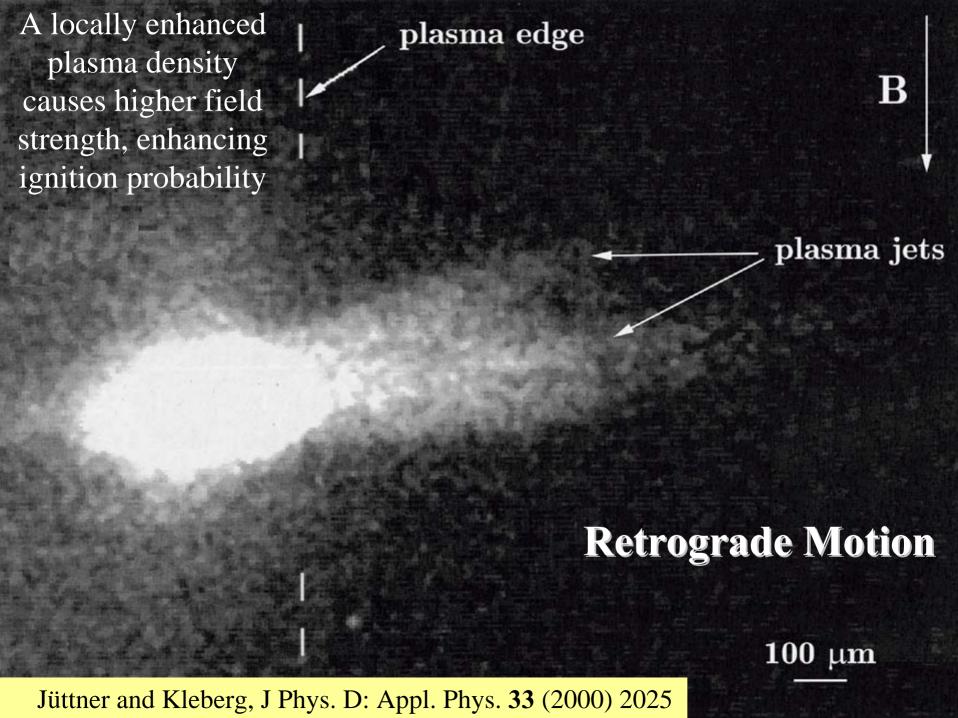




Fractal Sheath with "Holes"

- •sheath thickness scales scales with $1/\sqrt{n}$
- •no sheath but voltage drop in nonideal plasma of (exploding) emission centers: "holes" in sheath no flux to cathode





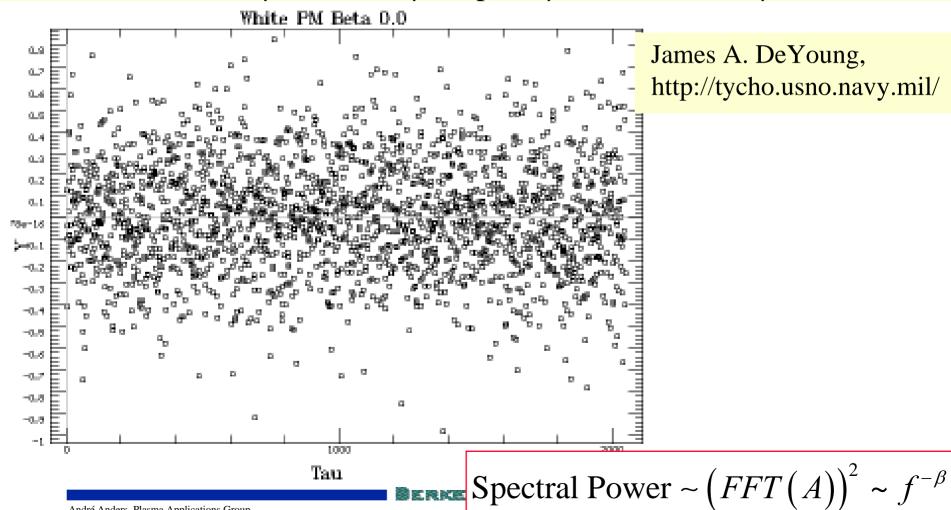


Noise – What Can We Learn?

Not all noise is equal!

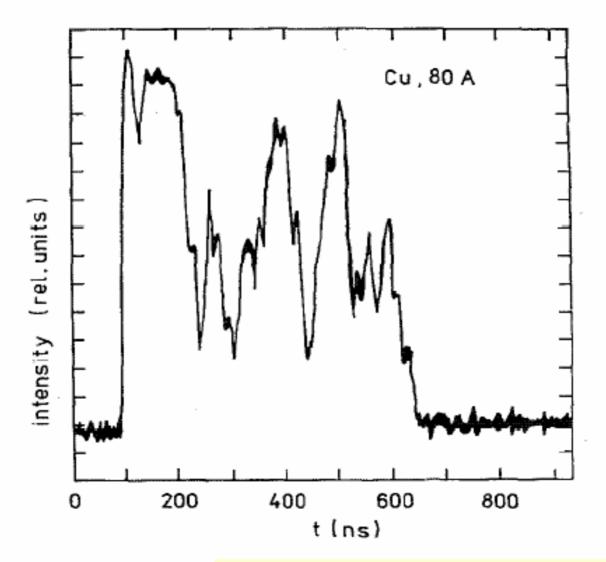
André Anders, Plasma Applications Group

"Colored" noise (β =0 white, β =1 pink, β =2 brown, and β >2 black)





Typical "Noise" of Plasma Parameters

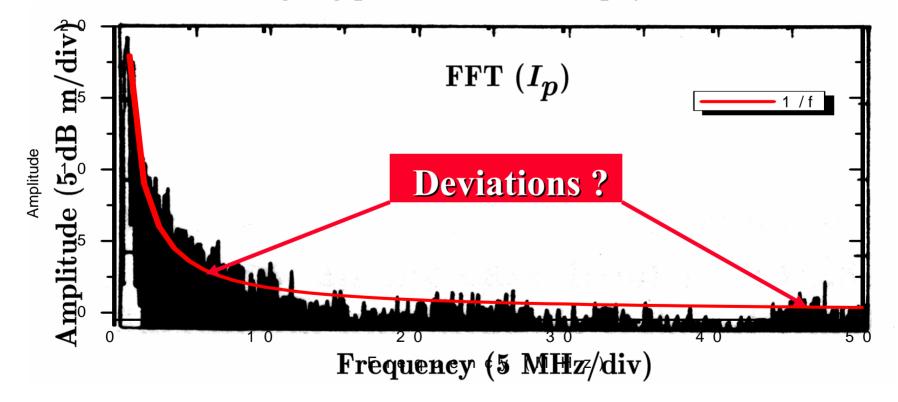


Anders, et al., J. Phys. D 25 (1992) 1591



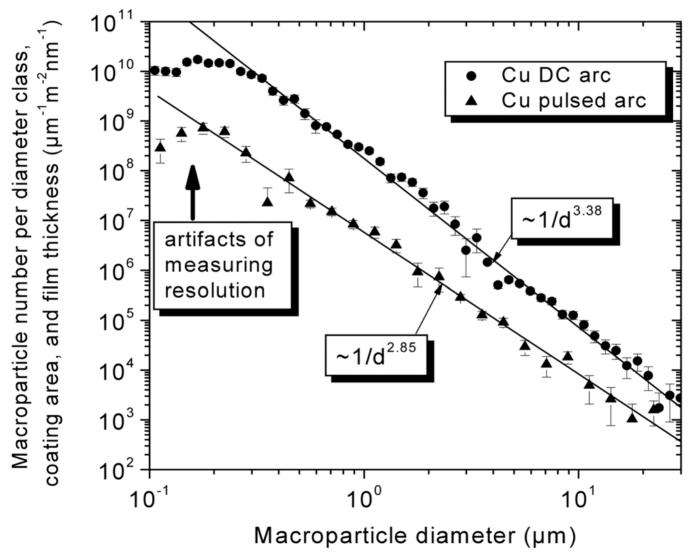
Fourier Transform Analysis

- □ In the limit of small current: one visible spot
- \Box 1/ f^2 (power) noise of light & ion current for f < 10 MHz
- one needs to use log-log presentation to see physics

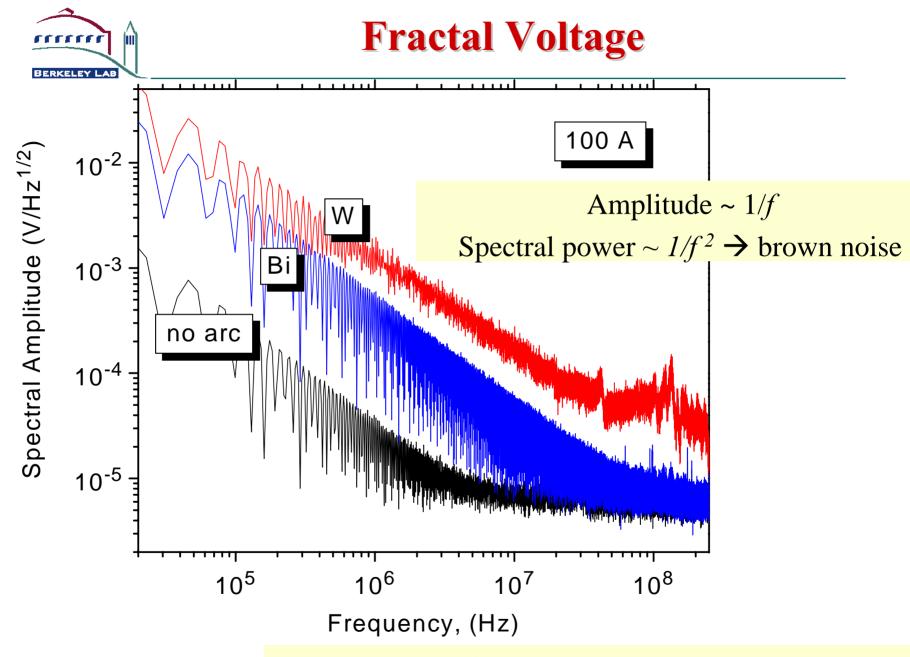




Fractal Macroparticle Distribution



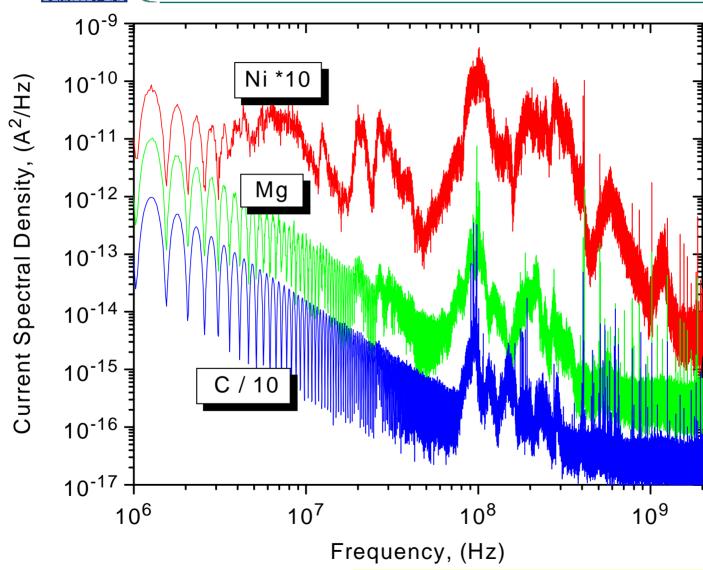
A. Anders, IEEE Trans. Plasma Sci. 33, no.5 (2005).



A. Anders, et al., Appl. Phys. Lett. 86, 211503 (2005).



"Ecton Cutoff" of Fractal Model



Anders and Oks, in preparation (2005).



Conclusions from Fractal Concept

- □ Cathodic arc has many self-similar features in time and space: fractal model is not only appropriate but a means a consolidating conflicting theoretical approaches
- □ Numerous power laws; giving linear slope when using log-log presentation; slope ,may be interpreted as a fractal dimension for the phenomenon
- \square For many of the noisy parameters, the spectral density is $\sim 1/f^2$, indicating "brown noise"
- □ Current noise shows 'ecton peaks' cutoff for a physical fractal model.

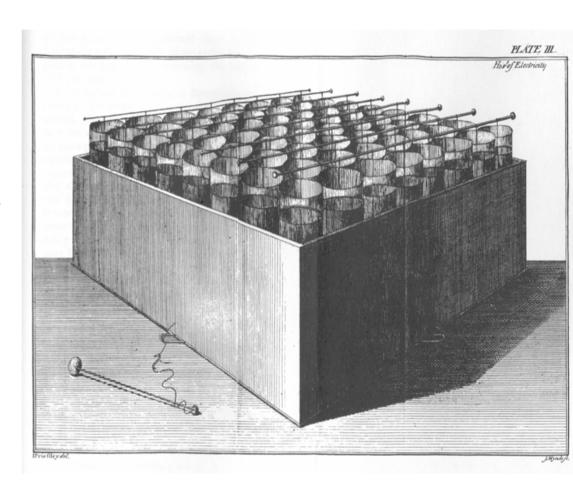


History



1766 - Joseph Priestley

- ☐ First cathodic arc coating (in air)
- ☐ discharge of a bank of Leyden jars through a brass chain
- □ arcs between each link of the chain
- □ deposit on glass is well adherent
- □ observed Newton's rings (oxide films)
- □ found black coating (copper oxide)



J. Priestley, The History and Present State of Electricity, London 1766

(on arc history) A. Anders, IEEE Trans. Plasma Sci. 31, 1052 (2003)

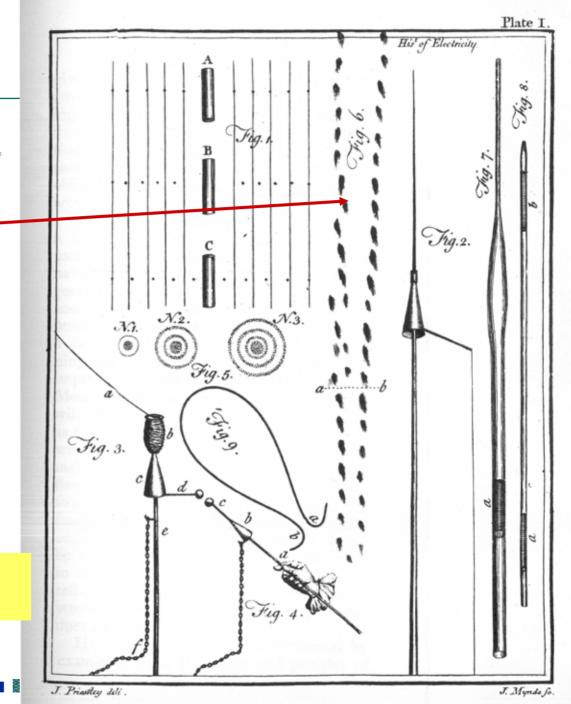


1766 - Joseph Priestley

Cathodic arc deposition

J. Priestley, The History and Present State of Electricity, London 1766

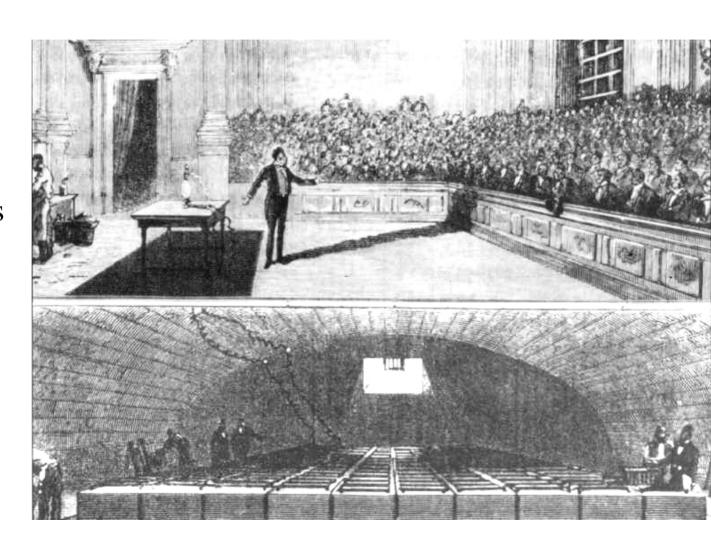
(on arc history) A. Anders, *IEEE Trans. Plasma Sci.* 31, 1052 (2003)





1802...1821 - Humphry Davy

- ☐ First short arcs in air that were fed by electrochemical battery (1802)
- □ Continuous arcs in air and in low-pressure vessels (1809)
- □ Arc demonstrations (1809?-1821)





1802/03 Vasilii Petrov

- ☐ First continuous arcs in air and at low pressure using an "enormous battery" of 4200 copper-zinc plates
- published only in Russian, his work was unknown or ignored

ИЗВБСТІЕ

0

ГАЛЬВАНИ - ВОЛЬТОВСКИХЪ ОПЫТАХЪ,

которые производиль

Профессорь Физики Василій Петровь,

посредствомь огромной наипаче баттереи, состоявшей иногда изь 4200 мьдныхь и цинковыхь кружковь, и находящейся при Санкт - Петербургской Медико - Хирургической Академіи.

ВЪ САНКТ-ПЕТЕРБУРГЪ;

Вь Типографіи Государственной Медицинской Коллегіи, 1803 года.



1877 - Arthur W. Wright

- □ Possibly a report on cathodic arc plasma deposition but more likely on pulsed sputtering:
 - □ inductive energy storage for pulsed arc
 - numerous cathode elements: Pt, Au, Co, Bi, Pd, Pb, Al,
 Sn, Mg, Zn, Cd, Ni, Co, Te, Fe
 - describes the different stability of films in atmosphere

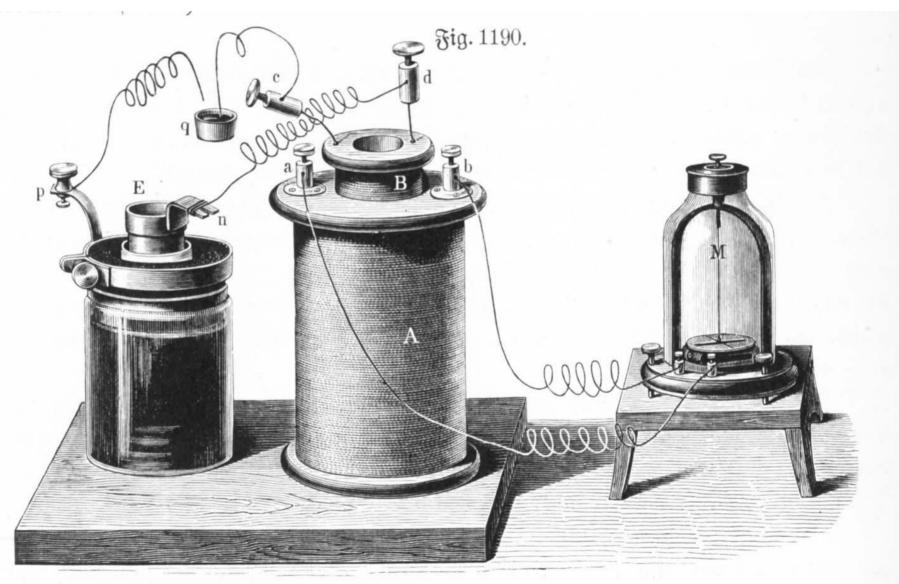
(unfortunately, no figure in paper)

A.W. Wright, American J. Sci. - Third Series, vol. XIII, no. 78 (1877) 49

R.L. Boxman, IEEE Trans. Plasma Sci. 29 (2001) 759-761



1877 - Arthur W. Wright





1888-1892: Edison's phonogram patent

•First patent application granted for arc plasma deposition limited to continuous arc that (ironically) turned out to be not useful 5

for coating of

original wax

phonograms

UNITED STATES PATENT OFFICE.

THOMAS A. EDISON, OF LLEWELLYN PARK, NEW JERSEY, ASSIGNOR TO THE EDISON PHONOGRAPH COMPANY, OF NEW JERSEY.

PROCESS OF DUPLICATING PHONOGRAMS.

SPECIFICATION forming part of Letters Patent No. 484,582, dated October 18, 1892.

Original application filed January 5, 1888, Serial No. 259,895. Divided and this application filed January 30, 1888. Renewed March 30, 1892. Serial No. 427,011, (No specimens.)

To all whom it may concern:

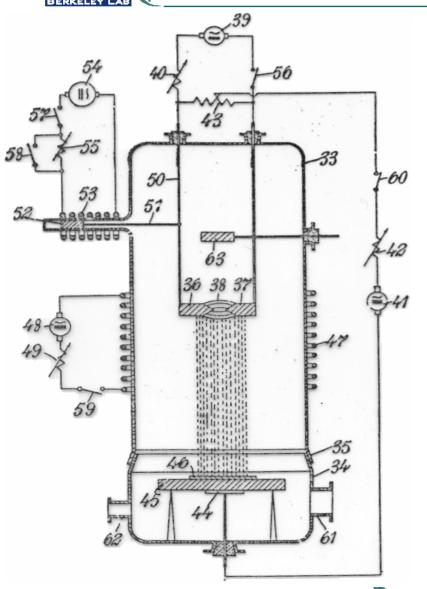
Be it known that I, THOMAS A. EDISON, of Llewellyn Park, in the county of Essex and State of New Jersey, have invented a certain new and useful Process for Duplicating Phonograms, (Case No. 751,) of which the follow-

covered by a more rapid process to give strength and body to the covering. A further covering of metal may be produced by electroplating a metal upon the vacuous deposit in the usual manner of electroplating, 55 or the vacuous deposit may be backed up by

By his attorney Syer & Leely



1939 - Burkhardt and Reinecke



□ Consumable
electrodes deposited
film onto biased or
unbiased substrates.

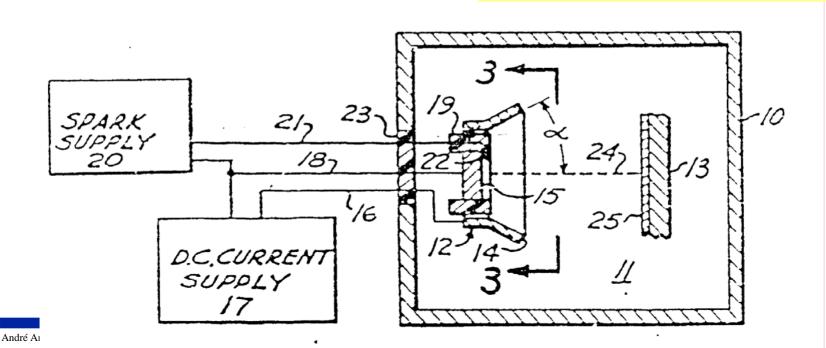
W. Burkhardt and R. Reinecke, US 2,157,478: Method of coating articles by vaporized coating materials.



1971 - Snaper

- □ Arc deposition process and apparatus.
- □ Cathodic arc source incorporated into a single devise.
- □ Insulator arc travel confinement.
- ☐ Line-of-sight process.
- ☐ Discrete anode (not chamber).

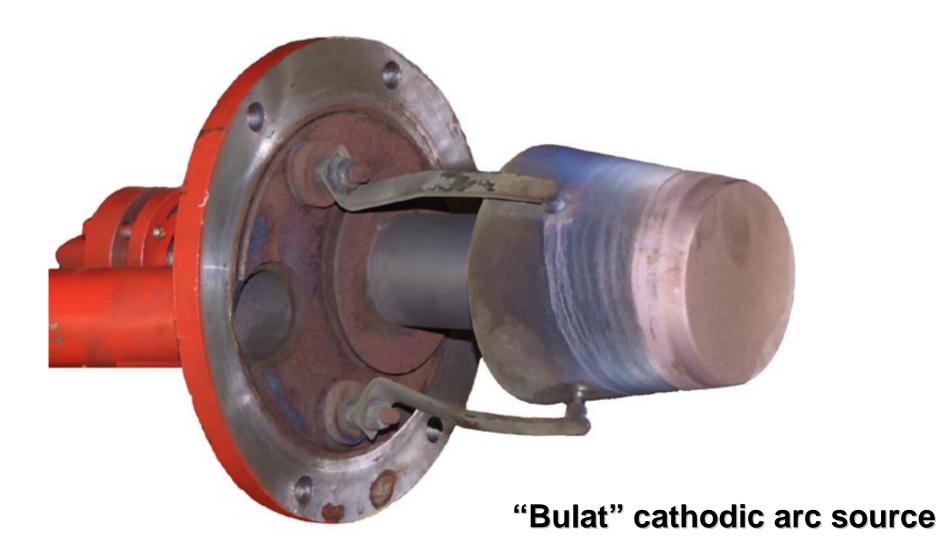
A.A. Snaper, (1974). US 3,625,848: Arc deposition process and apparatus.





Soviet Union in 1970s

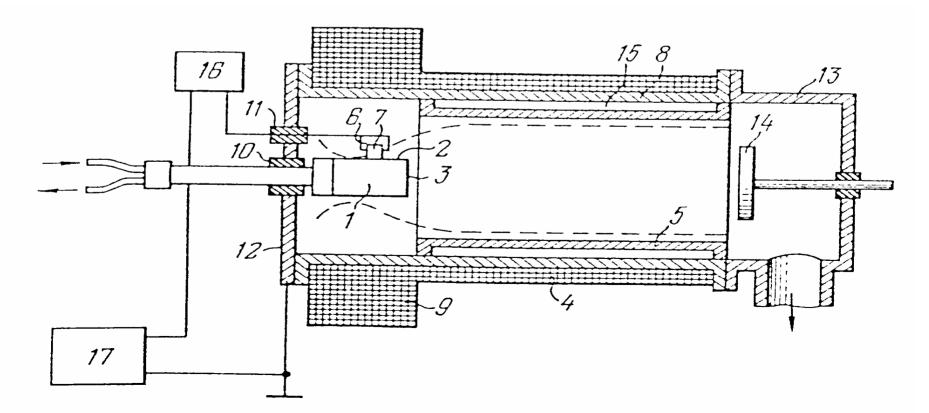
□ State-run development of eventually 10,000 arc source





1978, 1985 - Axenov et al.

- ☐ First major use of magnetic field control of coating particles leading the way to curvilinear devices for macroparticle control.
- □ Arc confinement on cathode face with magnetic fields.
- □ Chamber as anode.
- □ Line-of-sight process, and also non-line-of-sight processes.





Arc Plasma Sources Macroparticle Filters

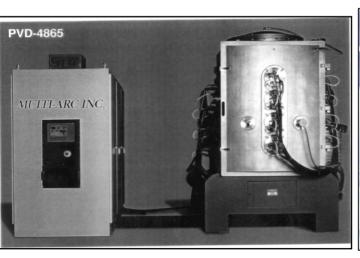




Batch versus Linear Processing

□ Batch Systems

- □ *low to moderate production volume*
- □ *lower cost to manufacture*
- □ good cycle to cycle inspection and maintenance of sources and inner chamber components (liners)
- greater operator interface handling substrates



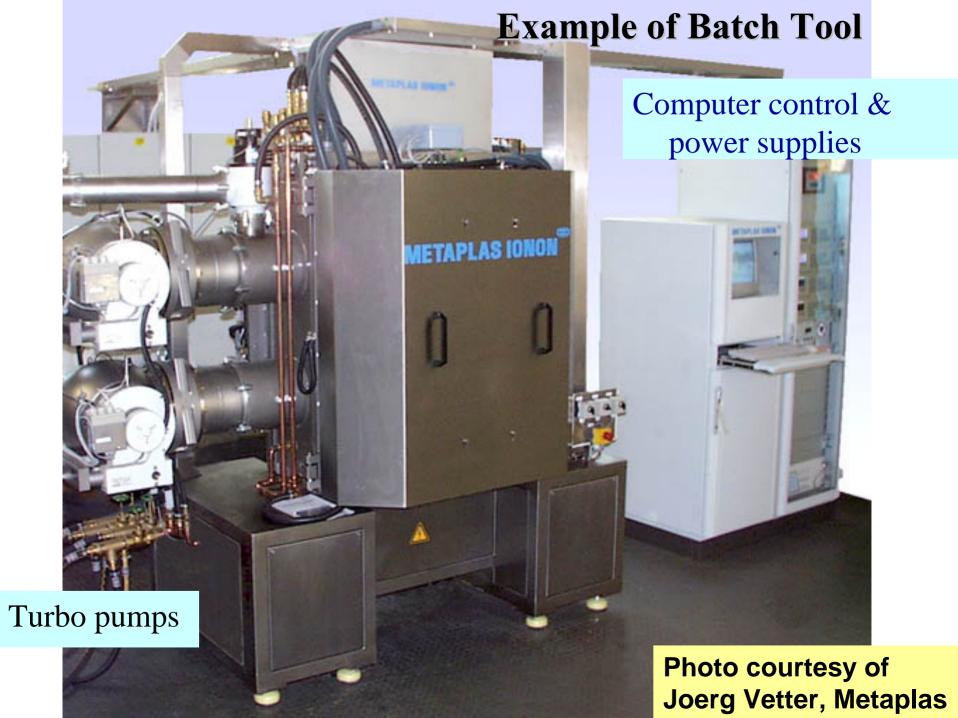




Ion Bond

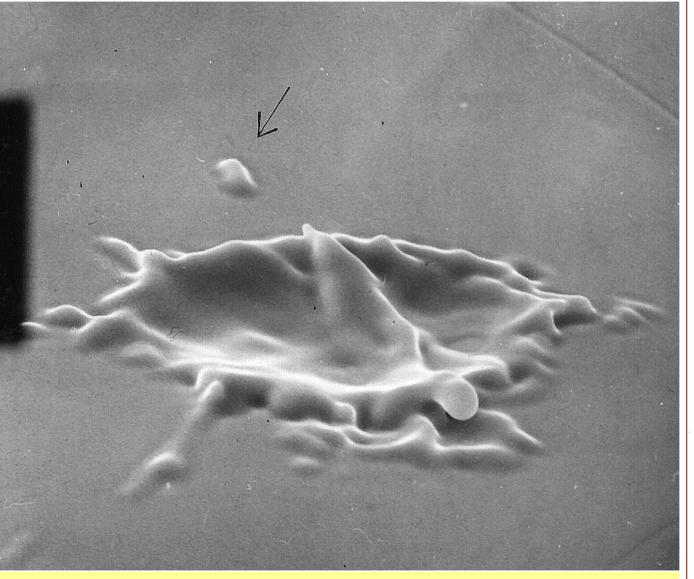
Hauser

Vergason



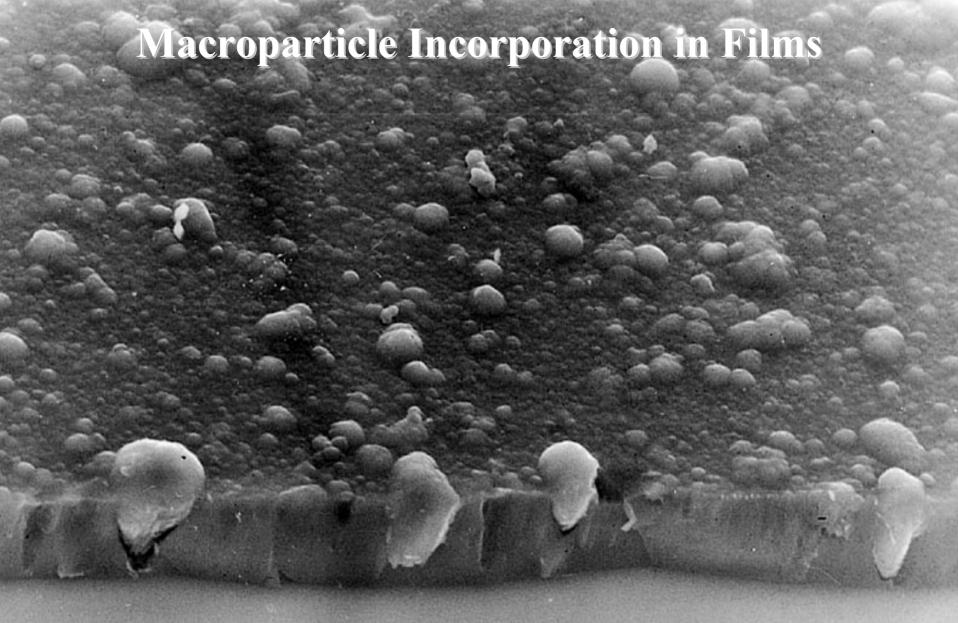


Macroparticle Generation



* ELECTRON **EMISSION** ION PRESSURE

10 ns, Mo, Figure courtesy of B. Jüttner

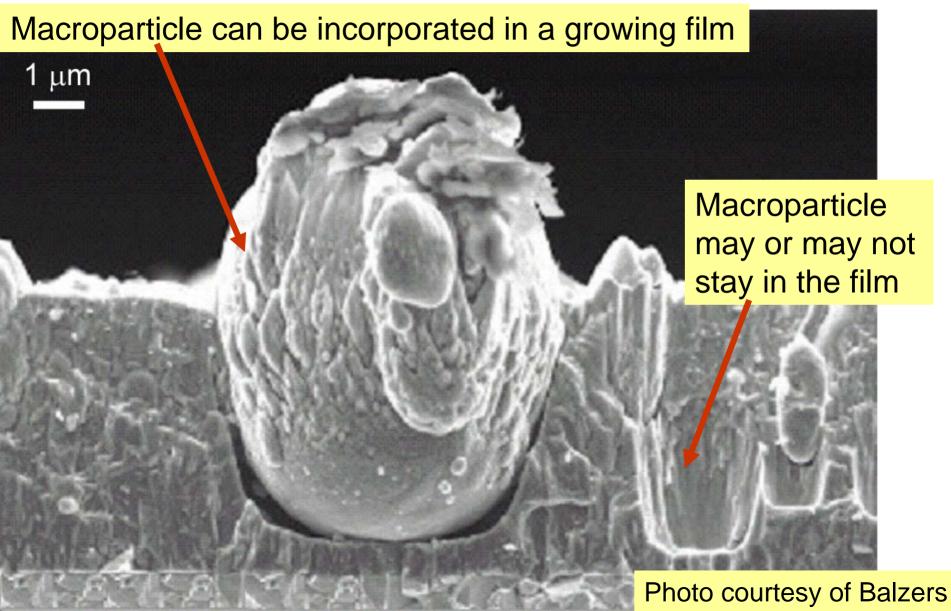


Courtesy of D. Drescher, see:D. Drescher, et al., Diamond Rel. Mat. 7 (1998) 1375

001722 10KV X5,000 21mm



Defect Formation by Incorporation of Macroparticles



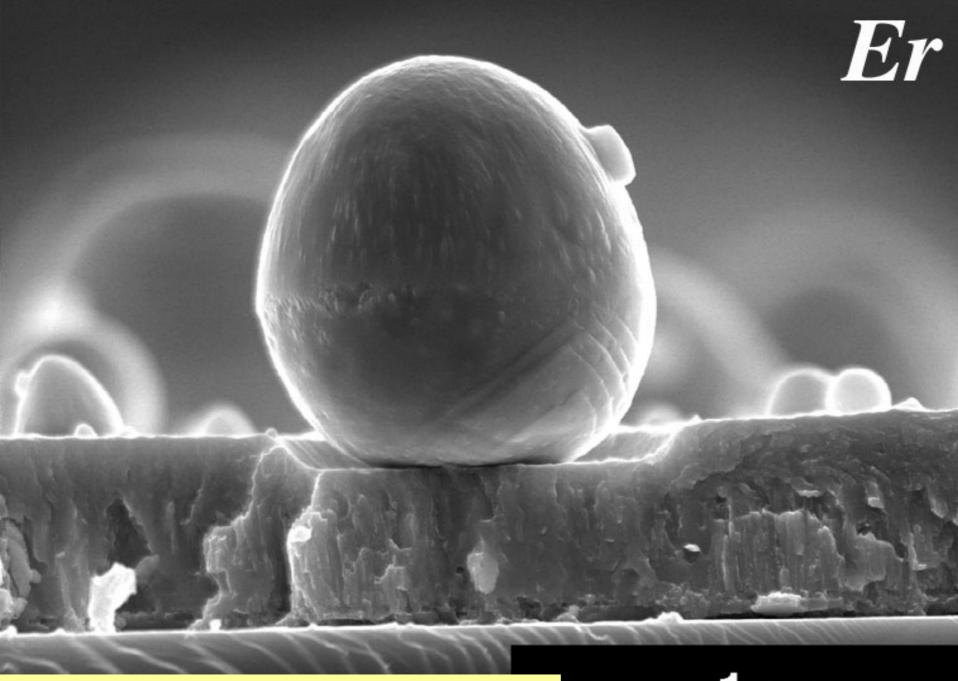


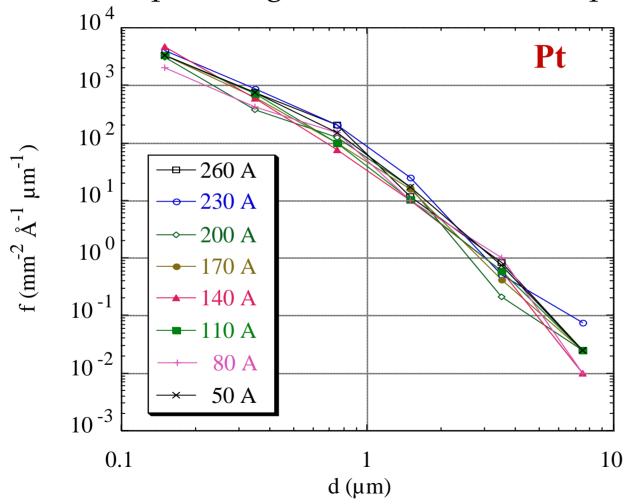
Photo courtesy of B. Wood, Los Alamos, NM

1 µm



Macroparticle Distribution

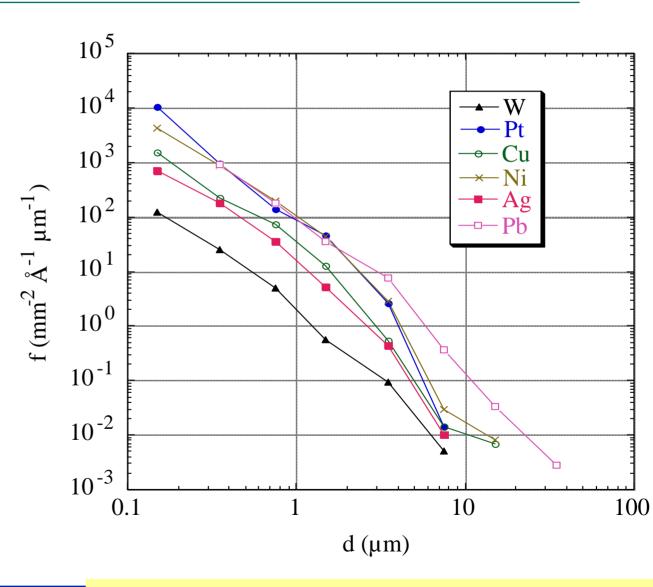
□ Macroparticle generation does not depend on arc current:

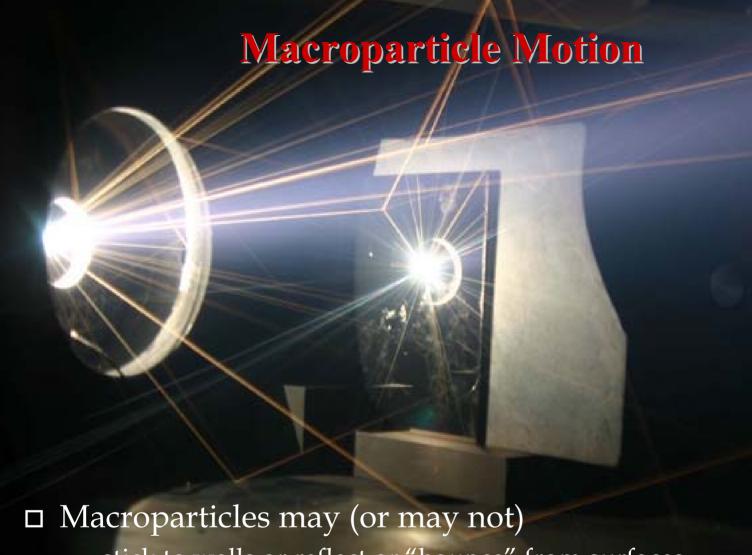




Macroparticle Distribution

- Materials of lower melting point have larger macroparticles
- □ Lower end of distribution is determined by instrumentation





- stick to walls or reflect or "bounce" from surfaces
- Fracture when hitting a surface

Example: Carbon macroparticle reflection and fracture

Macroparticle Motion

☐ Macroparticle reflect even from a liquid (!) surface in vacuum (liquid was vacuum pump oil)



Macroparticle Removal by Magnetic Filtering

ELECTRONS

- □ *Electrons are guided by magnetic field*: they gyrate around and along field lines $r_{c,e} = \frac{v_{\perp}}{\omega_{c,e}} = \frac{m_e v_{\perp}}{e B}$
- Electron gyration radius
- Electron motion perpendicular to field lines is facilitated by collisions; displacement is about one gyration radius

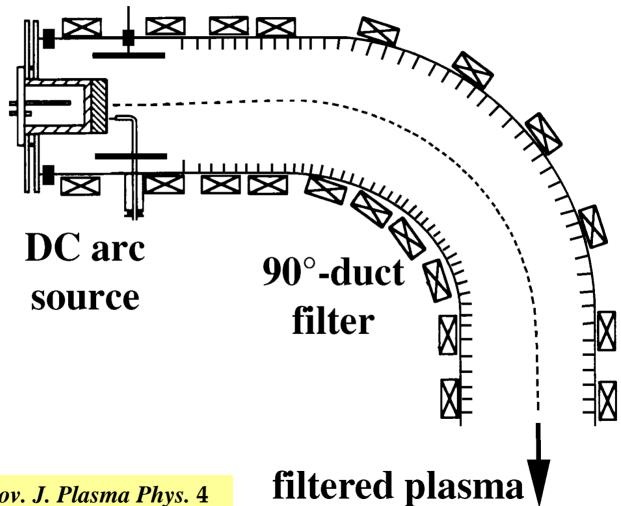
IONS

- Ions cannot be separated from electrons due to electric fields (plasma is quasi-neutral)
- □ *Ions are guided by electric potential minimum* along magnetic field lines

Transport of plasma in filters is a combined magnetic and electric mechanism



Classic 90° Duct



I.Aksenov et al., Sov. J. Plasma Phys. 4 (1978) 425-428



Out-of-plane, Double-bent Filter

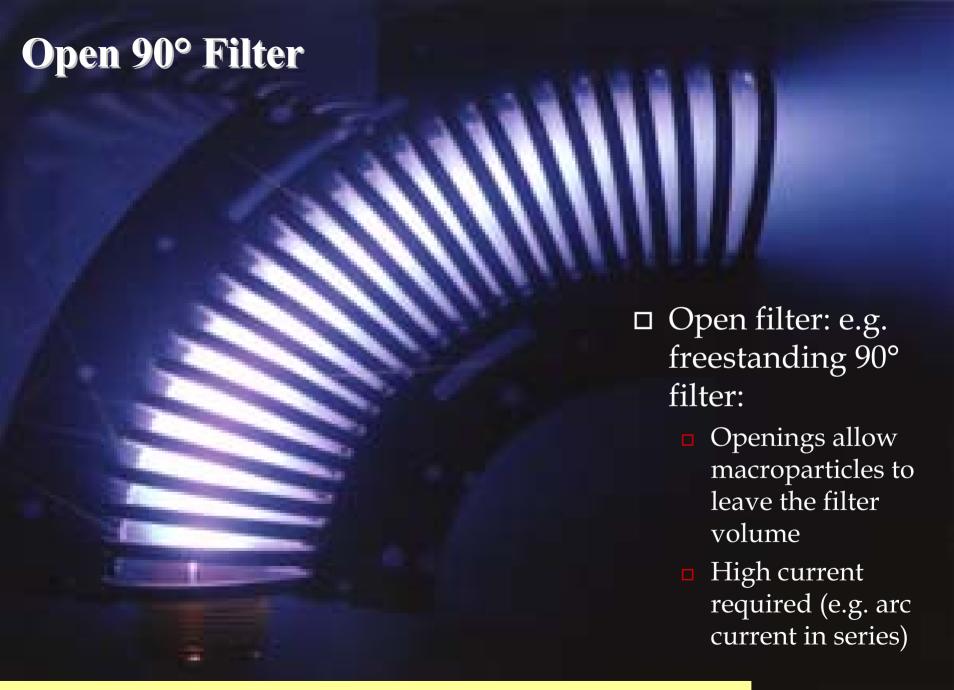
☐ Out-of-plane filter from Nanyang Technical University

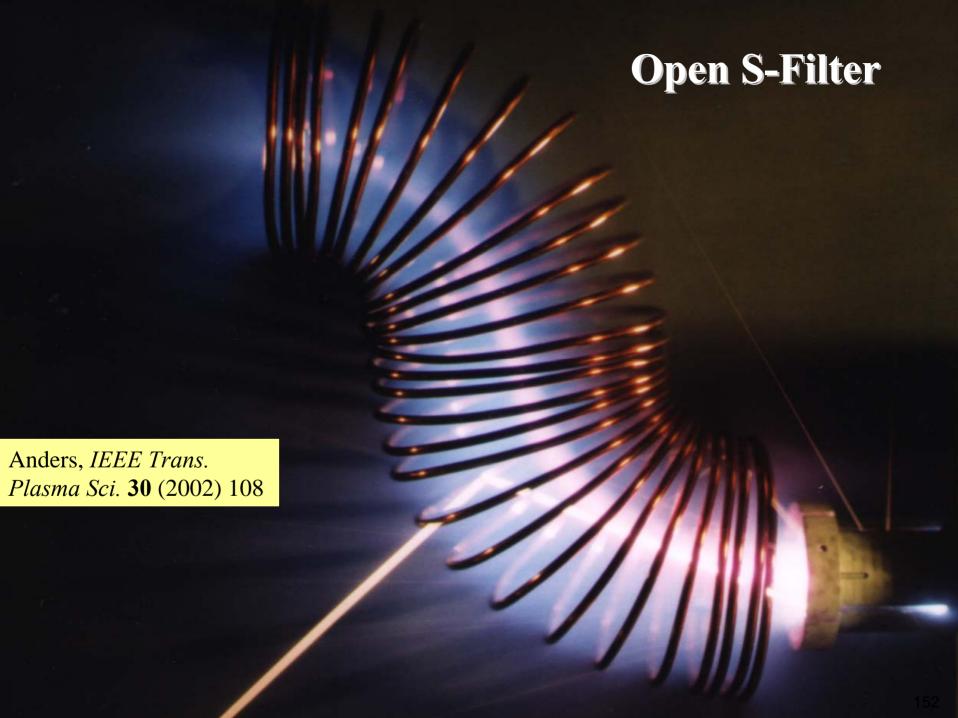
□ closed

□ commercial version

□ Shimadzu DLC-MR3CA

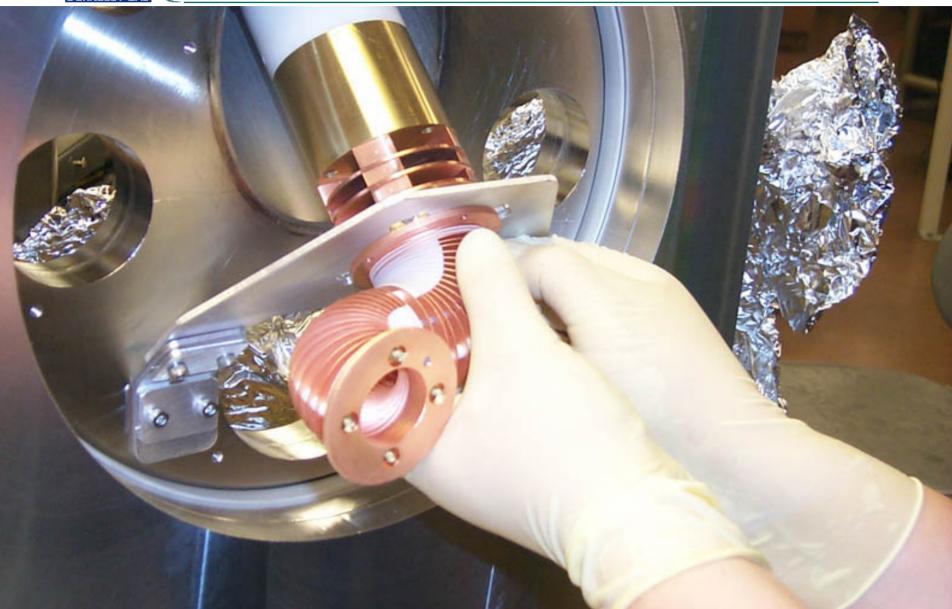








"Twist Filter": Open, Twisted S-Filter

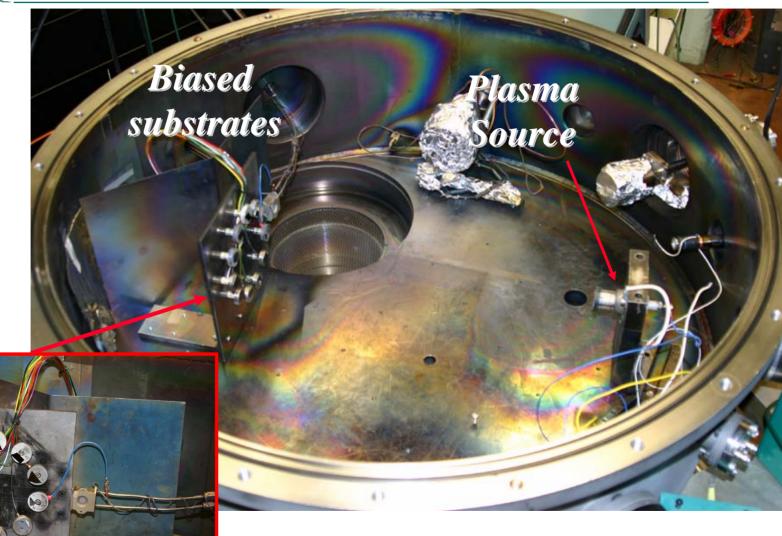




Energetic Condensation



Bias-(Energy!)-dependent Condensation

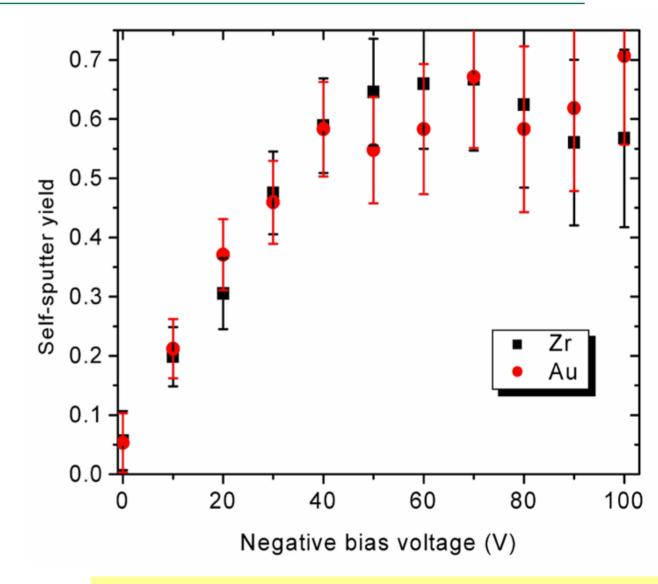


A. Anders, Appl. Phys. Lett., 85 (2004) 6137



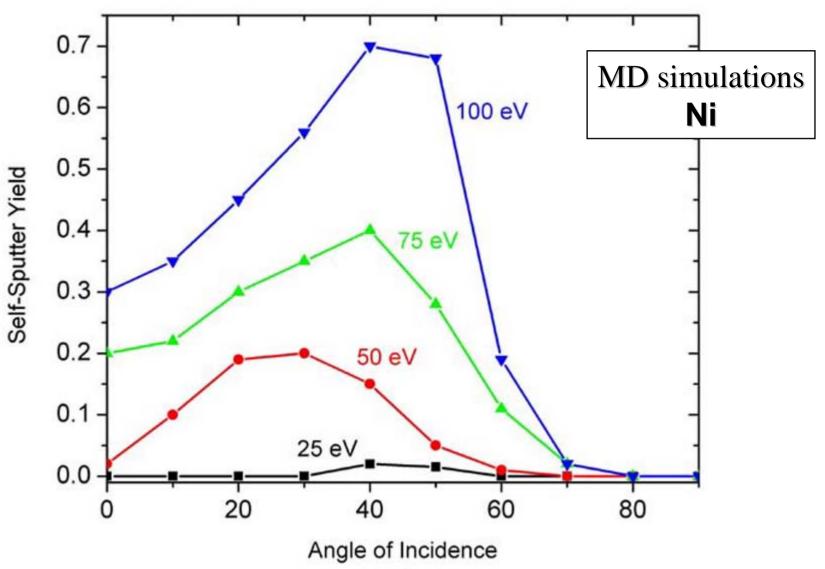
Bias-(Energy!)-dependent Condensation

- □ Result: at even moderate bias, film formation is reduced by self-sputtering
- □ Extreme examples: Au, Zr



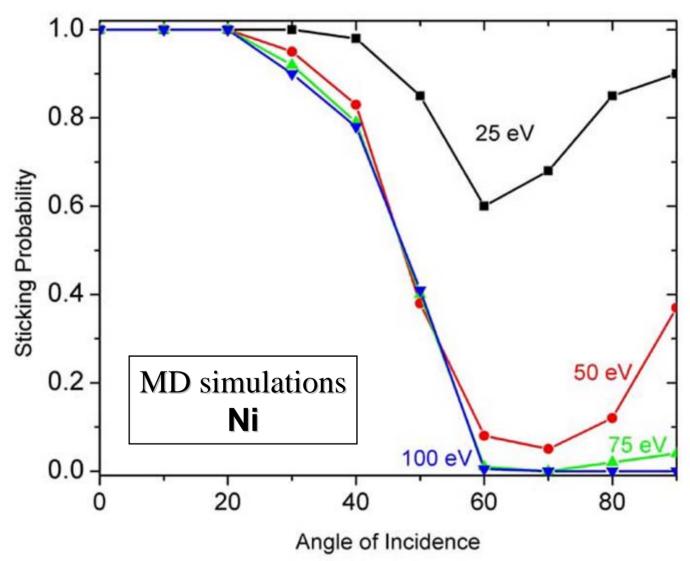


Self-Sputtering



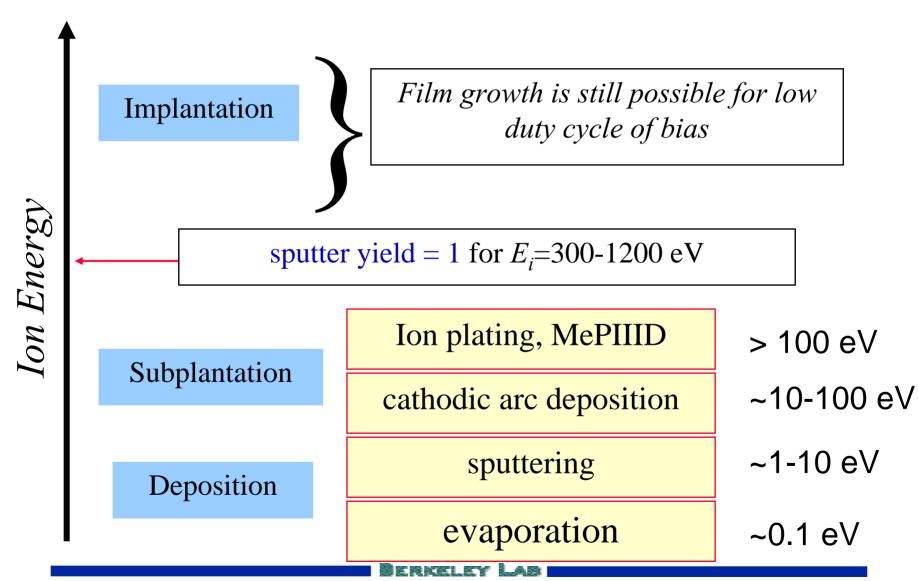


Sticking Probability





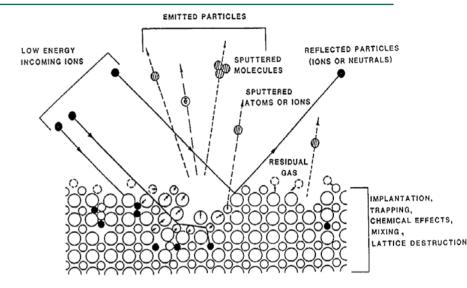
Energetic Relation Between Implantation and Deposition Processes





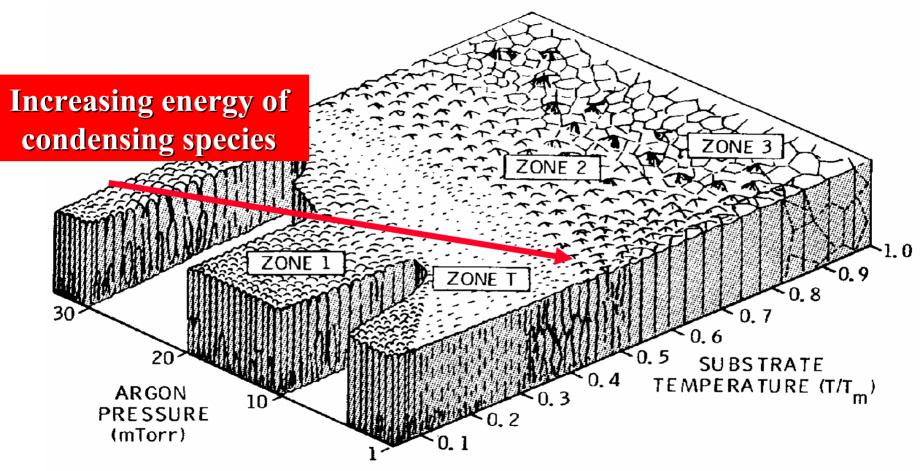
Plasma Deposition: Surface Processes Affected by Energy of Incoming Ions

- □ Sticking / reflection
- □ Sputtering
- □ Secondary electron emission
- □ Subplantation / implantation
- □ Surface diffusion
- □ Defect generation
- □ Phase changes, including precipitation
- □ heating
- □ adsorption/desorption of gas
- □ reaction with background gas atoms





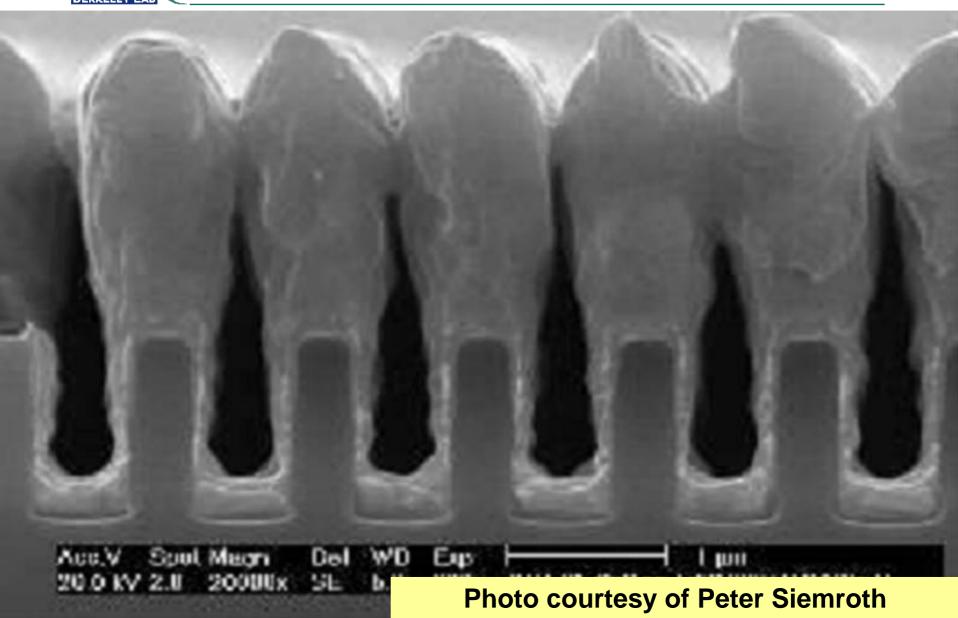
Structure Zone Diagram for Sputtered Films



Structure-zone diagram showing schematic microstructures of films deposited by cylindrical magnetron sputtering as a function of growth temperature and Ar pressure.

Example for non-energetic condensation: "Long-through-sputtering"

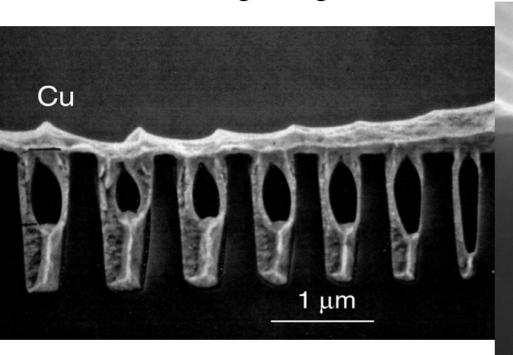
recere





Diffusion Barriers and Trench Filling

□ Trench filling using MePIIID with filtered copper arc plasma

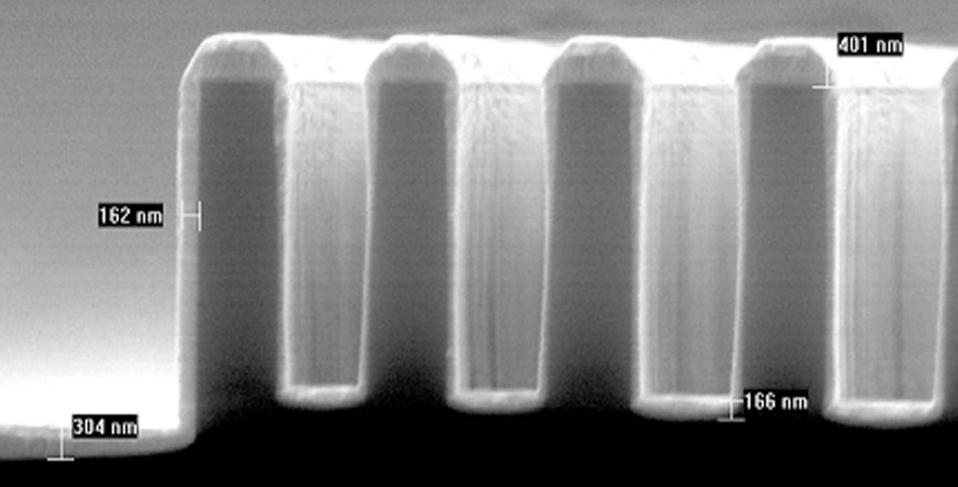


Cu

 $2.5 \mu m$

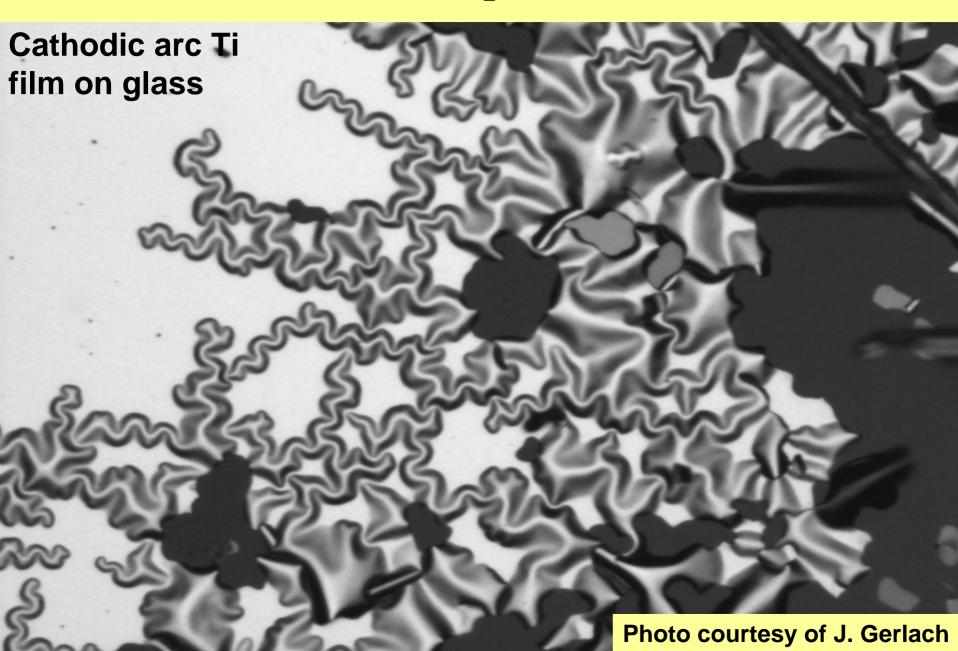
voids form if vapor / plasma does not have correct impact angle and energy perfect filling of trenches, only possible by effects of limited sticking and self-sputtering under energetic conditions!

More Ta barrier films
Pulsed high-current filtered Arc; Fraunhofer Institute (IWS, Dresden)



Acc.V Spot Magn Det WD F 2 μm 20.0 kV 2.0 13956x SE GK Ta_11 + 200nm HCA -350V 50/50 4.9 **Photo courtesy of Peter Siemroth**

Excessive Compressive Stress





Improvement of Film Adhesion by Bias

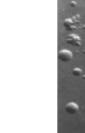
Effect of ion energy on the adhesion of Ag/YBa₂Cu₃O_x film on Si produced by MePIIID.

no bias

-200 V pulsed



- 1. sputter removal of contaminants
- 2. ion mixing
- 3. stress relieve



-2000 V pulsed

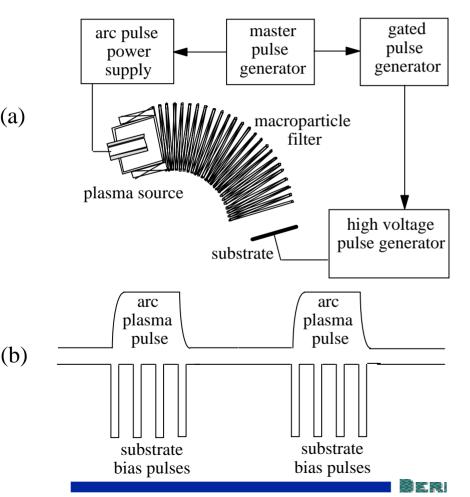
Beautiful MD simulations by Australian group, see, e.g., M. Bilek, et al., *IEEE Trans. Plasma Sci.* **31** (2003) 939

1 mm

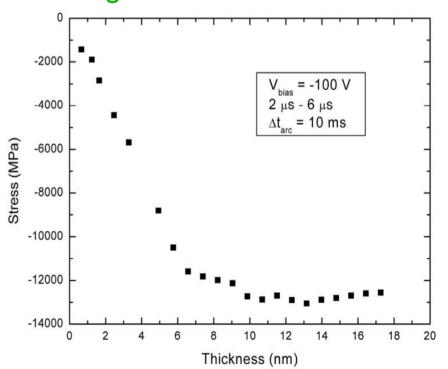


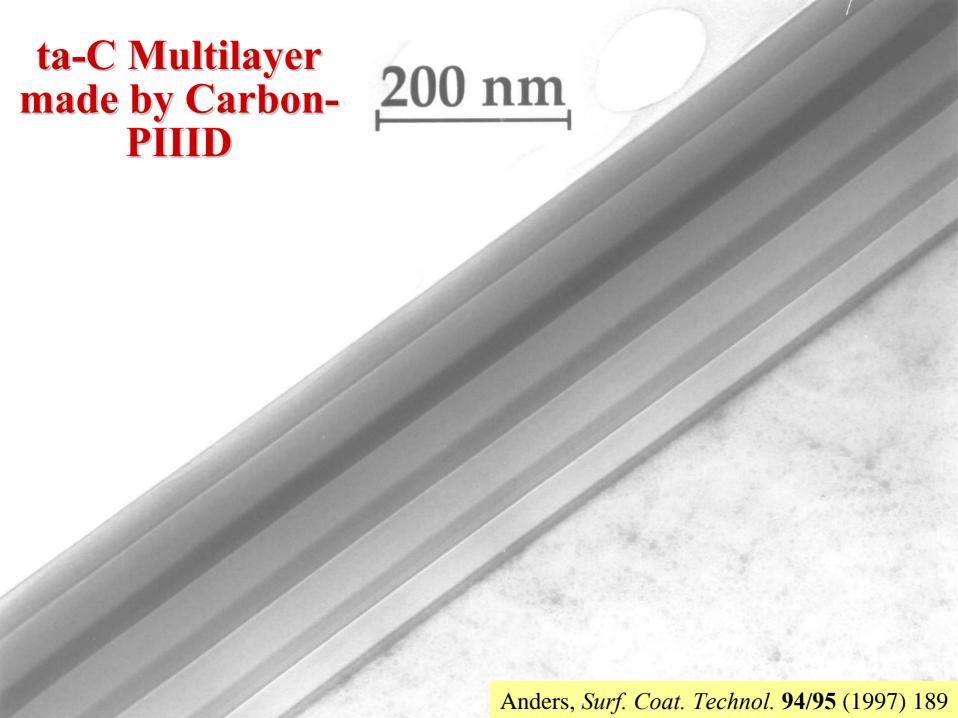
Buildup and Control of Intrinsic Stress in ta-C Films

Filtered pulsed cathodic arc and pulsed bias



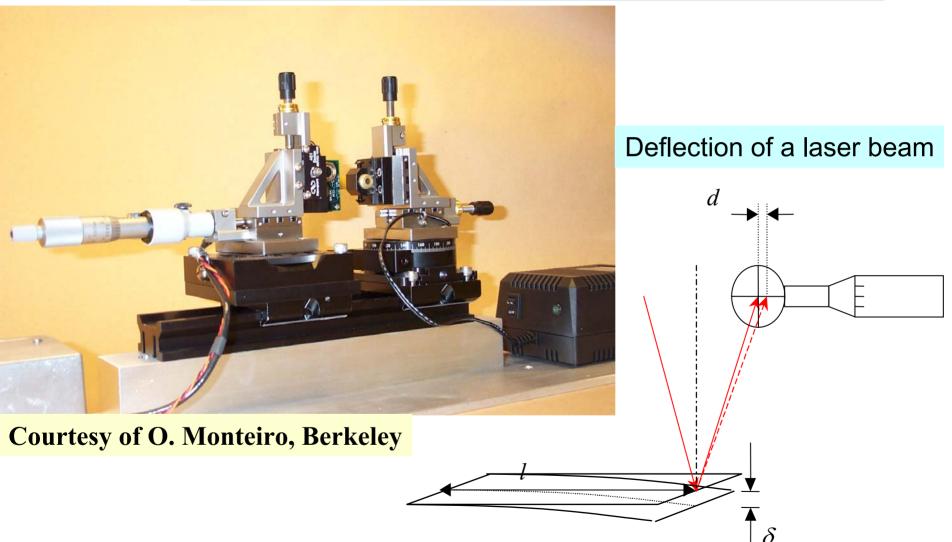
Pulsed bias voltage is used to change carbon energy and thereby bonding and stress in film



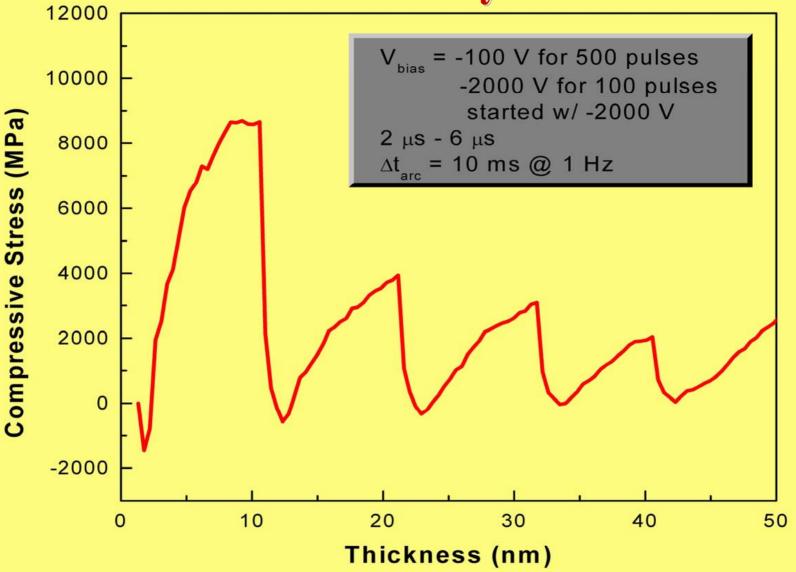




In-situ Monitoring of Stress for Stress Control by Thermal Spikes During Film Growth



Stress Relaxation by Ion Bombardment



M. P. Delplancke-Ogletree and O. R. Monteiro, *Diamond Rel. Mat.* 12 (2003) 2119



Conclusions

- □ Cathodic arc discharge is characterized by explosive electron emission, coupled to production of cathode plasma
- □ Cathode plasma properties follow *Cohesive Energy Rule*
- □ Cathode processes are stochastic and self-organized, fractal model is most appropriate; fractal properties are found both in temporal and spatial properties
- □ Perhaps the oldest plasma technology, yet "emerging technology" with disadvantages and advantages
 - □ Macroparticles which are addressed by filtering
 - □ high degree of ionization and energetic condensation to form dense films and nanostructures



In preparation:

Cathodic arc plasma deposition: From fractal spots to energetic condensation

Springer, New York 2006